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Diode like electron transfer in mixed monolayer assembly

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A phenomenon analogous to current rectification occurring in a diode could be demonstrated at the electrode/electrolyte interfaces constructed using a mixed monolayer configuration formed by the self assembly of decane thiol and thioctic acid. Two types of configuration have been described. In the first type (Configuration-1), diode like electron transfer is shown to occur in a ferrocene monocarboxylic acid functionalized mixed monolayer, in contact with the electrolyte containing potassium ferrocyanide. In the second type (Configuration-2), the functionalized mixed monolayer consists of two redox species ferrocene dicarboxylic acid and 1,4-diaminoanthraquinone linked through covalent linkage. This bilayer represents an electrochemical analogue of a diode and current rectification is observed.

1. Introduction

Formation of organized molecular assemblies at interfaces has been widely investigated in recent times as it offers vast scope for manipulating the interfacial architecture at the molecular level. The method of self-assembly offers a simple and elegant method to form organized monolayers. Self assembled monolayers (SAMs) serving as precision spacers between electrodes and reaction centers are used for resolving basic issues related to electron transfer kinetics.[1–7] SAMS are also being widely employed in the fields of molecular electronics,[8,9] molecular recognition[10,11] and catalysis.[12–14] One of the interesting aspects of working with SAMs is that it can lead to the preparation of miniaturized devices.

Currently, substantial research efforts are being directed towards the miniaturization of devices to nanoscale dimensions. The chemical modification of surfaces yields functionalized interfaces for molecular devices like rectifiers,[15,16] wires,[17,18] gates.[19,20] Modern molecular electronics began in 1974 when Aviram and Ratner[21] proposed a molecular rectifier based on an asymmetric molecular tunneling junction. Later on, the idea of making molecular rectifiers from bilayers of redox active polymers, for example Ru and Os–polypyridyl derivatives, ferrocenes and viologens dates back to the work of Murray and co-workers[22–25] and Wrighton and co-workers[26,27] in the early 1980s. In the latter half of the 1990s, electrochemical rectification was shown to occur on a ferrocene monolayer modified electrode in contact with an electrolyte solution containing sodium hexacyanoferrate[28] Diode like electron transfer across nanostructured films containing the redox ligand viologen, in contact with an electrolyte solution containing $[Ru(NH_3)_6]^{3+/2+}$ has also been demonstrated.[29] Nowadays sequential adsorption of polymer and semiconductor nanoparticles is being made use of, for the construction of self-assembled diode junctions. Efforts are also made in the direction of fabrication of molecular rectifiers made up of zwitterionic molecules, which have a donor–(pi-bridge)–acceptor or donor–(sigma-bridge)–acceptor configuration. Much progress has been reported[15,16,30–37] in this direction. Attempts to construct a biodiode of nm dimensions using bilayers of biomolecules on Au electrode have also been described.[38,39]

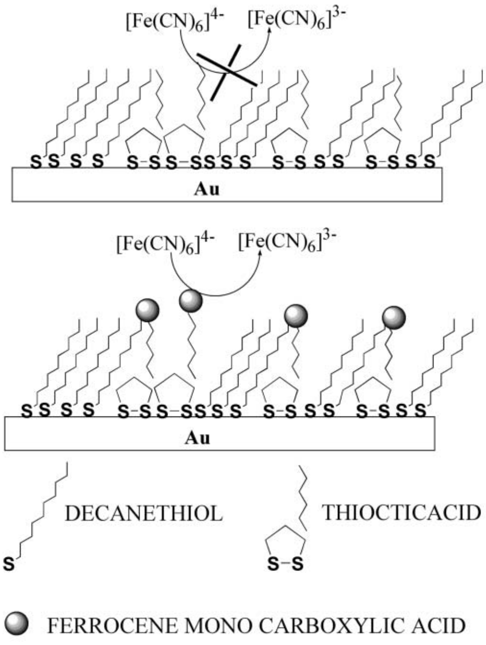
In this work, it is shown that an electrochemical rectification junction could be fabricated with the use of mixed monolayers from decane thiol and thioctic acid on gold substrate using the following two configurations.

1.1 Configuration-1

The mixed monolayer assembly is covalently coupled to ferrocene monocarboxylic acid through –COOH groups of thioctic acid. Configuration-1 in contact with an electrolyte solution containing potassium ferrocyanide exhibits rectification like properties (Scheme 1).

1.2 Configuration-2

Mixed monolayer assembly is covalently coupled to ferrocene dicarboxylic acid through –COOH groups of thioctic acid. This layer is further functionalized with 1,4-diaminoanthraquinone through amide-linkage between –COOH groups of ferrocene dicarboxylic acid and amino groups of DAAQ. The bilayer assembly (Scheme 2) thus constructed resembles a diode and exhibits rectification behaviour.



Scheme 1 Describing ferrocene monocarboxylic acid coupling to a (DT + TOA) mixed monolayer covered Au electrode (Configuration-1).

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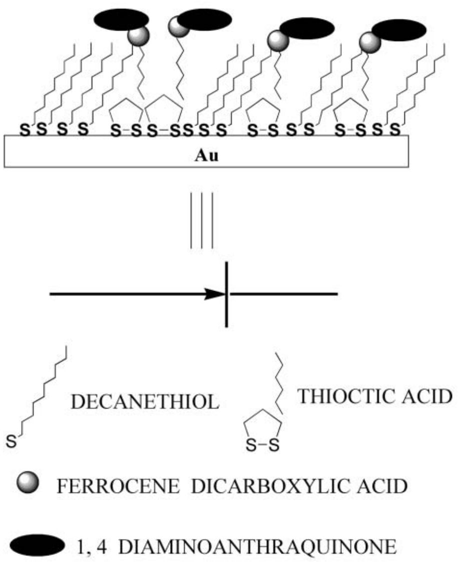


Scheme 2 Describing the coupling of ferrocene dicarboxylic acid followed by 1,4-diaminoanthraquinone to (DT + TOA) mixed monolayer covered Au electrode (Configuration-2).

2. Experimental

2.1 Materials

Decane thiol (DT) [96%], ferrocene monocarboxylic acid (FMC) [97%], ferrocene dicarboxylic acid (FDC) [96%], 1,4-diaminoanthraquinone (DAAQ) [90%], 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-p-toluenesulfonate (CMC) (all from Aldrich), potassium ferrocyanide (Merck) and thioctic acid (TOA) [98%] (SRL, India) were used as received. Buffer solutions (pH 4.5) were prepared using 0.1 M potassium hydrogen phthalate (AR, BDH) [99.9%] and sodium hydroxide (AR, Ranbaxy) [95%].

A gold disc of area 0.0314 cm^2 embedded in resin was used as the substrate for the formation of the mixed monolayer. Before modification gold discs were thoroughly cleaned using emery sheets of grade (4/0,5/0) using alumina slurry followed by sonication in Millipore water for two minutes. The polished electrodes were then cycled in 0.5 M H_2SO_4 at low scan rates between −0.2 and 1.0 V (*vs.* Hg/Hg_2SO_4) for 5 minutes as a pre-treatment to get a reproducible surface. The reproducibility of the surface is checked by running a cyclic voltammogram of the 5 mM $K_4[Fe(CN)_6]$ in Na_2SO_4 which exhibits good reversible features with $\Delta E_p = 60$ mV. Gold substrates standardized using the above procedure were used for modification.

2.2 Formation of the mixed monolayer

Gold substrate was dipped in DT overnight, removed and rinsed with ethanol and dried in the presence of N_2. The substrate was then kept immersed in 20 mM TOA solution in ethanol for three hours. Afterwards, the substrate was removed, rinsed in ethanol and dried in the presence of N_2. This results in the formation of a mixed monolayer of DT and TOA on the Au surface.

2.3 Construction of Configuration-1

Mixed monolayer modified gold substrate modified as above was treated with 0.02 M CMC in phthalate buffer (pH 4.5) for one hour and then transferred to a solution containing 2 mM FMC in ethanol for two hours. After this treatment the electrode was rinsed in ethanol and dried in the presence of N_2 and characterized using cyclic voltammetry.

2.4 Construction of Configuration-2

Mixed monolayer modified gold substrate was treated with 0.02 M CMC in phthalate buffer (pH 4.5) for one hour and then transferred to a solution containing 2 mM FDC in ethanol for two hours. Afterwards, the substrate was rinsed with ethanol and dried in the presence of N_2. The treated gold substrate was again subjected to the above CMC treatment followed by dipping in DAAQ (2 mM) solution to get the bilayer-modified electrode.

2.5 Characterization of the modified substrates

Modified Au substrates were characterized by cyclic voltammograms carried out with the help of Potentioscan (POS 88, Wenking, Germany) and X-Y/t Recorder (Rikadenki, Japan). Modified gold substrate is used as the working electrode. Hg/Hg_2SO_4 and a Pt foil served as the reference and the counter electrodes respectively. All the potentials mentioned in this study are referred to the above reference electrode.

3. Results and discussion

Fig. 1 presents the cyclic voltammetric response in phthalate buffer of the gold substrate modified by DT (a), TOA (b) and DT + TOA (c). The voltammograms are featureless indicating no electroactivity in the potential range used. The double layer capacitance values for the three modified electrodes were estimated from the CV's and presented in Table 1. The capacitance current for the DT-covered electrode is significantly low as expected from its low C_{dl} value (4.8 μF cm^{-2}), which shows its good insulating properties. On the other hand, the thioctic acid monolayer exhibits a slightly greater capacitance current (C_{dl} = 9.5 μF cm^{-2}) as expected from its disulfide ring structure, whose steric factor and the tendency to breaking of the disulfide bond result in a monolayer that has defects and is

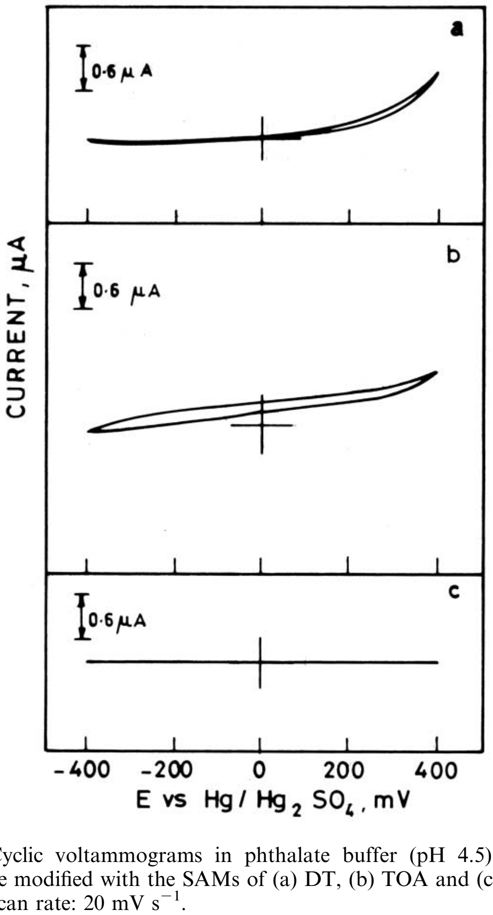


Fig. 1 Cyclic voltammograms in phthalate buffer (pH 4.5) of Au electrode modified with the SAMs of (a) DT, (b) TOA and (c) DT + TOA. Scan rate: 20 mV s^{-1}.

Table 1 Double layer capacitance (C_{dl}) of the monolayer-modified Au electrodes (from voltammetric data)

Electrode	C_{dl}/μF cm^{-2}
Au/DT	4.8
Au/TOA	9.5
Au/(DT + TOA)	2.5

less compact. However, the mixed monolayer configuration yields a highly compact and insulating monolayer as seen by the suppression in the capacitance current to a greater degree (C_{dl} = 2.5 μF cm^{-2}).

Fig. 2 shows the cyclic voltammetric response for 5 mM $K_4[Fe(CN)_6]$ in phthalate buffer (pH 4.5) on Au electrodes modified with DT (a), TOA (b), and DT + TOA (c). As indicated earlier by their capacitance values, the monolayers exhibit very good blocking properties towards ferrocyanide electron transfer. Complete blocking is observed in the case of the mixed monolayer configuration. Hence the mixed monolayer assembly represents a highly compact and pinhole free film, an ideal prerequisite for the building of bilayer configuration.

Fig. 3 represents the cyclic voltammogram obtained for the modified electrode of Configuration-1, consisting of the mixed monolayer assembly covalently coupled to FMC molecules. The modified electrode shows a quasi-reversible response with a monolayer of coverage of 9.90 × 10^{-11} mol cm^{-2} and its E^0 (formal potential obtained as the mean of anodic and cathodic peak potentials) value was found to be −0.04 V. The voltammogram exhibits a ΔE_p corresponding to 80 mV. The ideal value of $\Delta E_p = 0$ is not obtained since the FMC molecules are covalently coupled through the –COOH groups of TOA. Moreover, the mixed monolayer assembly of DT and TOA acts like an insulating barrier and the electron transfer is facilitated only through thioctic acid linkage. Hence the kinetics are slowed down. This kind of slowing down of electron transfer has been reported earlier in similar systems.[40–42]

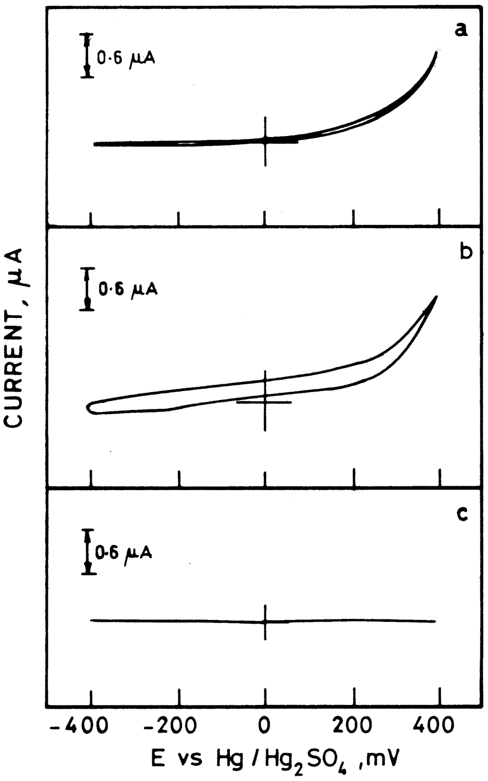


Fig. 2 Cyclic voltammograms for 5 mM $K_4[Fe(CN)_6]$ in phthlate buffer (pH 4.5) on Au electrode modified with the SAMs of (a) DT, (b) TOA and (c) DT + TOA. Scan rate: 20 mV s^{-1}.

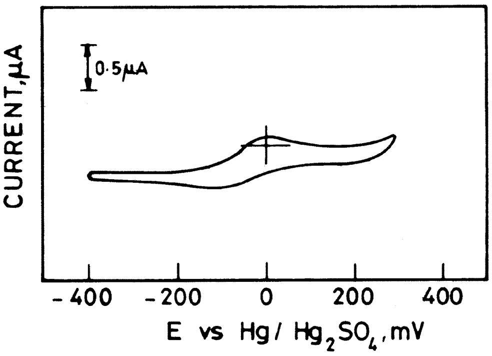


Fig. 3 Cyclic voltammogram in phthalate buffer (pH 4.5) of the Au electrode modified with a mixed monolayer of (DT + TOA), further coupled with FMC molecules (Configuration-1). Scan rate: 20 mV s^{-1}.

Fig. 4 represents the cyclic voltammograms obtained with the modified electrode Configuration-1, in contact with different concentrations of $K_4[Fe(CN)_6]$ in phthalate buffer (pH 4.5). Direct electron transfer between substrate gold and ferrocyanide ion, leading to the oxidation of the latter is suppressed everywhere on the monolayer except at those sites where the redox active FMC molecule is present. At these sites the immobilized redox active ferrocene moiety facilitates mediated electron transfer from solution-phase ferrocyanide, thereby leading to its oxidation. The shape of the cyclic voltammogram obtained reflects this fact.

It is pertinent to note from Fig. 4 that no cathodic peak corresponding to ferricyanide reduction was observed on the reverse scan. For comparison, the cyclic voltammetric response of 4 mM potassium ferrocyanide on bare gold electrode is given as an *inset* in Fig. 4. This behaviour corresponds formally to current rectification (*i.e.* current is made to pass in the forward direction but not in the backward direction). The absence of a cathodic peak for ferricyanide reduction and the fact the anodic peak is shifted positive of that for ferrocyanide oxidation at an unmodified electrode suggest strongly that ferrocyanide oxidation is occurring in a mediated fashion *via*

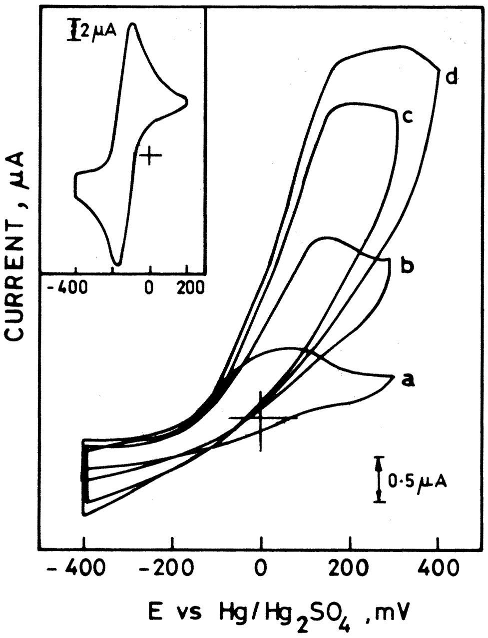


Fig. 4 Cyclic voltammograms of (DT + TOA) mixed monolayer modified Au electrode further coupled to FMC (Configuration-1) in phthalate buffer (pH 4.5) containing different concentrations of $K_4Fe(CN)_6$. (a) 0.3424 mM, (b) 0.6802 mM, (c) 1.048 mM, (d) 1.3422 mM. Scan rate: 20 mV s^{-1}. *Inset* shows the cyclic voltammogram of 4mM $K_4Fe(CN)_6$, on bare Au electrode.

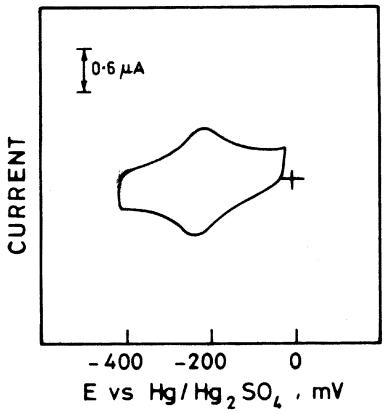


Fig. 5 Cyclic voltammogram in phthalate buffer (pH 4.5) of the Au electrode modified with a mixed monolayer of (DT + TOA) and further coupled with DAAQ. Scan rate: 20 mV s^{-1}.

electrogenerated ferricenium with ferrocyanide. The $E^{0'}$ value of 5 mM $K_4[Fe(CN)_6]$ in phthalate buffer on a bare Au electrode was independently estimated to be −130 mV (figure not shown). The E^0 value for the immobilized FMC species is −0.04 V (*cf.* Fig. 3). The relative formal potentials for the immobilized FMC and the dissolved ferrocyanide suggest that ferrocenium should be a strong enough oxidant to oxidize ferrocyanide (which is thermodynamically favourable), but FMC should not be a strong enough reductant to reduce ferricyanide (the reverse reaction being thermodynamically unfavourable). The oxidation of ferrocyanide by the mediation of the immobilized FMC is further confirmed by the observed increase in oxidation current with the increase in ferrocyanide concentration in solution.

Fig. 5 presents the cyclic voltammogram obtained for the modified electrode consisting of the mixed monolayer assembly (DT + TOA) coupled to DAAQ. The modified electrode shows a quasireversible response with a coverage of 4.9 × 10^{-10} mol cm^{-2} and its $E^{0'}$ value was found to be −230 mV *vs.* Hg/Hg_2SO_4. The voltammogram exhibits a ΔE_p corresponding to 20 mV. This experiment shows that the $-NH_2$ groups of DAAQ molecule could be linked to COOH groups of TOA through covalent linkage.

Fig. 6 presents the cyclic voltammogram obtained with the modified electrode of Configuration-2. Curve (a) shows the voltammetric response of the electrode after the first stage of modification, *viz.* the mixed monolayer being covalently coupled to ferrocene dicarboxylic acid (FDC). The cyclic voltammogram shows quasi-reversible features, the kinetics of electron transfer being controlled by the linking group (thioctic acid moiety). The $E^{0'}$ of the immobilized species under identical experimental conditions is found to be 110 mV and the modification corresponds to a surface coverage of 5.077 × 10^{-10} mol cm^{-2}. Curve (b) depicts the cyclic voltammetric response obtained with the bilayer assembly consisting of FDC in the first layer and DAAQ in the second layer.

The direct access of DAAQ to the electrode surface is prevented by the compact and pinhole-free mixed monolayer assembly. The bilayer assembly consists of two redox species with two different $E^{0'}$ values. This configuration is analogous to the donor–(sigma-bridge)–acceptor assembly envisaged by Aviram and Ratner[21] and they represent the organic counterparts of the p–n junction that are suitably aligned to permit electron transfer in one direction only. The expected result is reflected in the cyclic voltammogram (curve b), which shows that the oxidation of the DAAQ is mediated through FDC molecules in the first layer. The absence of the cathodic peak for the DAAQ reduction and the fact that the anodic peak is shifted positive of that for DAAQ oxidation at an unmodified electrode both strongly suggest that DAAQ oxidation is occurring in a mediated fashion *via* the electro-generated ferrocenium ion. The surface coverage calculated from curve b is found to be of the same order as the sum of the individual monolayer coverages due to FDC and DAAQ (Fig. 6(a) and Fig. 5).

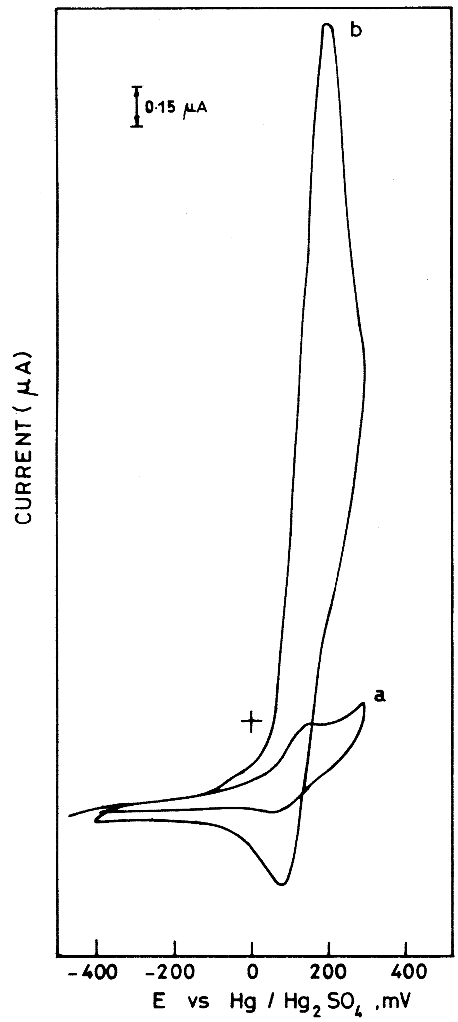


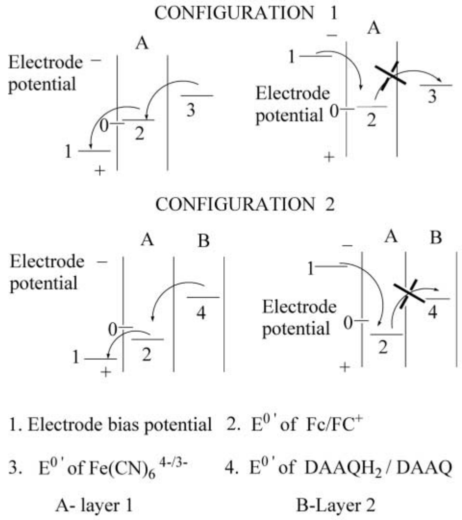
Fig. 6 Cyclic voltammograms of (DT + TOA) mixed monolayer modified Au electrode further coupled to FDC initially and DAAQ subsequently (Configuration-2) in pthalate buffer (pH 4.5). Scan rate: 20 mV s^{-1}. (a) before DAAQ coupling and (b) after coupling DAAQ.

Further, the $E^{0'}$ value of DAAQ immobilized on a bare Au electrode in phthalate buffer was estimated to be −230 mV. The relative formal potentials [of immobilized DAAQ and FDC molecules; *cf.* Fig. 5 and 6(a)] suggest that the forward mediation reaction is thermodynamically favourable and the reverse reaction is highly unfavourable. Hence the bilayer assembly shows the typical characteristics of a rectification junction or a diode and hence is called an electrochemical analogue of a diode.

Scheme 3 represents the principle of how the rectification is possible in the mixed monolayer assembly described in this work. The scheme clearly explains how redox species with different E^0 values are suitably arranged in a self-assembled monolayer configuration. When the electrode potential is biased in the positive direction, oxidation current is recorded. When the electrode potential is shifted to a negative value, the potential energy level of the second layer is not suitably placed for back electron transfer. Hence rectification should be observed.

4. Conclusion

This work describes in detail how a mixed monolayer could be fabricated using the phenomenon of self-assembly. Electron transfer is permitted only at sites, which are linked with



Scheme 3 Describing schematically the current rectification behaviour at the modified electrode surfaces.

ferrocene carboxylic acid. Further functionalization of the monolayer with the second redox species resulted in the bilayer assembly, which exhibits a property analogous to current rectification in a diode.

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