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Note on the voltammetry of ferrocene carboxylate in aqueous solution

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Abstract

Cyclic voltammetry of ferrocene dicarboxylate in aqueous solutions at high pH, in the presence of oxygen, showed evidence of an EC' mechanism where the oxidised form of ferrocene dicarboxylate reacts with HO_2^- , which had been produced at a lower potential. However, an analogous experiment with ferrocene carboxylate yielded a cyclic voltammogram with a post peak following the anodic peak for ferrocene carboxylate. The reason for the post peak is not clear but may be due to a delay in the reaction between the oxidised form of ferrocene carboxylate and HO_2^- . © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cyclic voltammetry; Oxygen reduction; Ferrocene carboxylate; Ferrocene dicarboxylate

1. Introduction

Ferrocene and its derivatives have formed the basis of many mediation systems especially in second-generation mediator systems with enzymes [1,2], a popular case in point being glucose oxidase [3]. The electrochemistry in non-aqueous solutions has been characterised to the extent that ferrocene has been used as a reference couple with respect to which potentials are quoted [4]. It has been used for this purpose for the electrochemistry of oxygen in DMF, DMSO and acetonitrile [5]. The purpose of this note is to describe preliminary work on the electrochemistry of ferrocene carboxylate (FcA) in aqueous solution in the presence of oxygen.

2. Results and discussion

As a comparison, the electrochemistry of 1,1'-ferrocene dicarboxylate (FcDa) is shown in Fig. 1 both in the presence of air and in a solution which has been bubbled with oxygen. The electrochemical arrangement has been reported previously [6] and the main difference between this work and previous work is that the cyclic voltammetry is carried out at slower sweep rates. In the presence of oxygen the following reduction occurs [7]:

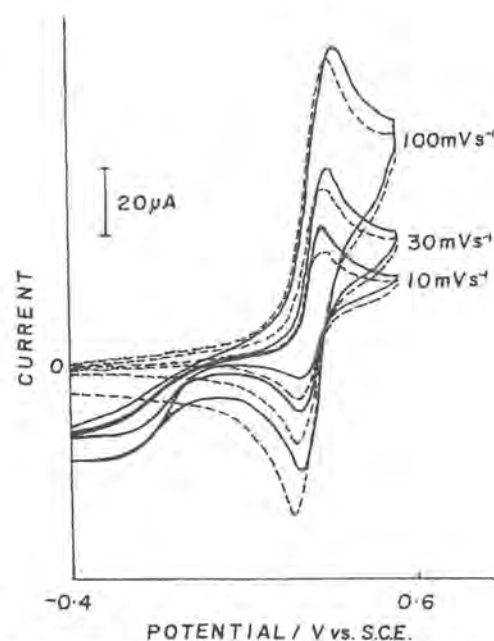
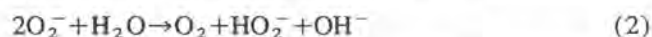


Fig. 1. Cyclic voltammograms of FcDa (10^{-2} mol dm^{-3}) in borate buffer (pH 10) at a glassy carbon electrode: (---) in air; (—) solution bubbled with oxygen for 10 min. Sweep rates 100, 30 and 10 mV s^{-1} .



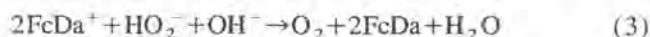
At the initial potential (-0.4 V versus SCE), the reduction of oxygen occurs and the superoxide reacts immediately with water to yield HO_2^- and, thus, the oxygen reduction reaction can be represented as the sum of reactions (1) and (2). At the initial potential (-0.4 V versus SCE), oxygen is reduced

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at the working electrode. As the potential is swept the FcDa is oxidised. Ferricenium dicarboxylate then reacts with the reduced form of oxygen as follows:



thus regenerating FcDa in an EC' mechanism [8]. As such the forward peak increases and the reverse peak decreases. The oxidation peak for FcDa is 0.368 V versus SCE. In the case of ferrocene carboxylate (FcA) shown in Fig. 2 the oxidation peak is 0.277 V versus SCE and it would be reasonable to imagine a similar behaviour between ferricenium carboxylate and HO_2^- . However, the cyclic voltammetry of FcA in the presence of air is not as simple (Fig. 2). It can be seen at slower sweep rates that there is a post peak subsequent to the oxidation peak of FcA. This peak occurs at 0.317 V versus SCE; it shifts to more positive potentials with increasing sweep rate and its magnitude decreases. There are a few points to mention about this post peak:

(a) It occurs to the same extent at glassy carbon, Pt and Au. This implies the process is not a simple adsorption process that varies depending on the electrode material. It can only be seen clearly at slow sweep rates of 20 mV s^{-1} or less and there is no corresponding reduction peak. At faster sweep rates the reduction of ferricenium outruns the rate of the subsequent chemical reaction.

(b) The post peak disappears when the solution is degassed with nitrogen and its magnitude increases with increasing concentration of FcA up to 10 mM and/or oxygen where the solution is saturated with oxygen.

(c) The post peak is still present when enough β -cyclodextrin is added (20 mM) to the solution to ensure that FcA is complexed [6]. The formal potential of the complex is more positive than that of uncomplexed FcA and the current decrease indicative of complexation, but the post peak is still present. When complexed with β -cyclodextrin, only the dissociated FcA reacts at the electrode since the complexed FcA is shielded because of its inclusion in the cavity and will not have direct contact with the electrode for electron transfer to take place. The mediation therefore occurs when FcA has left the cavity, become oxidised and before it is recomplexed with β -cyclodextrin.

(d) The post peak does not appear when FcA is not present; there is no anodic current corresponding to the oxidation of HO_2^- in the background electrolyte alone at the potential where the post peak occurs.

(e) In the presence of FcA, the post peak does not occur at lower pH, for example in 0.1 M KCl, 0.1 M LiClO_4 , even when bubbled with oxygen. The $\text{p}K_a$ for FcA is 4.2 and thus it should completely dissociate under these conditions. At this pH the O_2 is not reduced at the initial potential (0.0 V versus SCE).

(f) No post peak occurs when the cyclic voltammogram of FcA is run in acetonitrile when H_2O is deliberately added to a concentration of 6.3 mol dm^{-3} . The addition of water causes a shift in the formal potential of FcA from which it

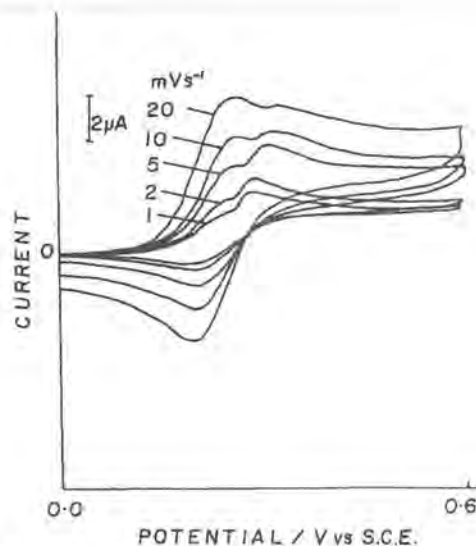


Fig. 2. Cyclic voltammograms of FcA ($10^{-3} \text{ mol dm}^{-3}$) in Na_2HPO_4 (0.2 M, pH 9.2) at a gold working electrode in the presence of air. Sweep rates are indicated in the plot.

can be deduced that there is one water molecule complexed to each ferrocene carboxylate in acetonitrile [9].

(g) The post-peak magnitude increases as the initial potential is made more negative (from 0.0 to -0.4 V versus SCE) since there is a greater quantity of HO_2^- present for reaction with the oxidised form of FcA. The magnitude of the post peak increases with the time that the cell is held at 0.0 V versus SCE prior to sweeping the potential. It is interesting to compare the differences in voltammetry between mono- and disubstituted ferrocene. The presence of a post peak implies that there is a delay in a reaction which could be an induction period before the reaction takes place or characteristic of the EC' reaction.

Fig. 3 shows an overlay of a cyclic voltammogram of FcA in a degassed solution and a solution that is saturated with oxygen. It can be clearly seen that the post peak appears on

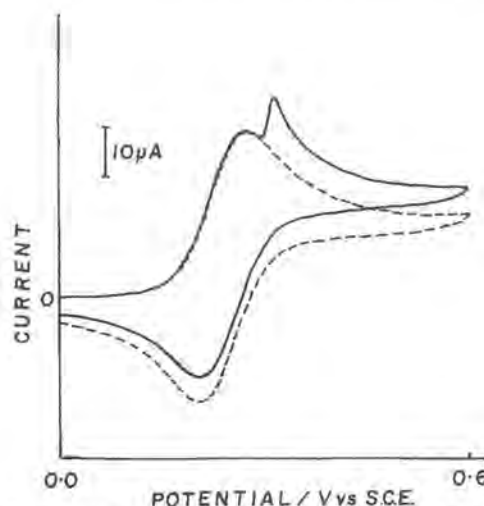


Fig. 3. Cyclic voltammograms of a saturated solution of FcA at a gold electrode in $0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{HPO}_4$ (pH 9.2) bubbled with nitrogen (---) and bubbled with oxygen (—). Sweep rate 10 mV s^{-1} .

the decay of the first peak without affecting the magnitude of the first peak. A clearer idea of the mechanism would be gained from the study of the effect of varying FcA concentration, O₂ concentration and pH, and perhaps examining other derivatives of ferrocene.

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