

Chemically modified electrode based on an organometallic model of the [FeFe] hydrogenase active center

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Abstract

A dithiolate-bridged diiron complex containing succinimide ester has been grafted on glassy carbon electrodes modified with either amine or aminophenyl groups. Covalent attachment of the complex through amide binding is confirmed by the linear dependence of the reduction peak current on the voltammetric scan rate. Attachment using the aminophenyl-modified electrode leads to better behaved cyclic voltammograms. The effect of addition of acid on the voltammetric response is also reported.

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1. Introduction

A great deal of interest has been devoted to the production of hydrogen, considered as the one of the main energy sources for the future [1]. On the other hand, a wide variety of microorganisms use hydrogenase enzymes to efficiently catalyze the production and uptake of hydrogen, i.e. $2\text{H}^+ + 2\text{e}^- = \text{H}_2$. In recent years, chemical models of the organometallic active center of iron-only hydrogenases ([FeFe] H₂ases) have been extensively studied with the hope of finding transition metal-based catalysts [2–6]. Dinuclear iron complexes [Fe₂-(SRS)(CO)₄L₂] (R = C₃H₆, C₆H₄, C₂H₄NR', R' = *p*-bromobenzyl; L = CO, PR₃'', CN⁻) have been shown to catalyze the electrochemical proton reduction [7–12]. Unfortunately, these organometallic complexes are only soluble in organic solvents, while the use of water as a

proton source for hydrogen production is mandatory. One possibility to overcome this issue is to attach the dinuclear iron complexes on the electrode surface to achieve a so-called chemically modified electrodes (CMEs). There are many examples of self-assembled monolayers (SAMs) on gold surface, where surface modification is accomplished either by synthesizing a molecule with a pendant alkanethiol group or more conveniently by the chemical modification of a thiol monolayer [13]. But in the case of a hydrogen evolution electrode, it is, however, desirable to attach the organometallic moiety more firmly than is possible through the use of SAMs. Very recently, Geiger and coworkers [14] have reported that cobaltocenium could be attached to an electrode through the reduction of its diazonium salt. Chemically modified carbon surface can also be achieved by coupling of the carboxylic acid containing glassy carbon (GC) surface with an amine having electrochemically reactive moiety [15]. But, Savéant and coworkers [16] have reported a better method of modification of carbon surface, which involves the grafting of

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4-aminophenyl groups on the electrode surface. In addition, amide bonding can be achieved by the reaction of substrates having *N*-hydroxysuccinimide (NHS) ester functionality with a modified electrode having amine groups on its surface [17].

We here report the covalent binding of a new dinuclear iron complex relevant to the [FeFe] hydrogenase chemistry and the further investigation of the glassy carbon grafted electrode in acid-containing electrolyte.

2. Experimental

Electrochemical measurements were conducted in a conventional glass cell with a gold wire as counter electrode and either a SCE or an Ag/Ag⁺ electrode as reference electrode ($E_{1/2}[\text{Fc}^{+/0}] = 0.15 \text{ V vs. Ag/Ag}^+$). The GC electrode was grafted with aminophenyl groups by two voltammetric cycles at 0.05 V s^{-1} between 0.8 and -0.3 V vs. SCE in $0.1 \text{ M H}_2\text{SO}_4 + 5 \text{ mM}$ nitrobenzenediazonium tetrafluoroborate (Scheme 1, step (a)). The attachment of the nitrophenyl groups and their reduction to aminophenyl groups was confirmed by comparing the voltammetric response with that in the earlier reported procedure [16]. The aminophenyl-modified electrode was then thoroughly rinsed with water and sonicated for 10 min in acetone. A control CV in MeCN + Bu₄NPF₆ showed no reversible events in the range 0.0 to $-2.5 \text{ V vs. Ag/Ag}^+$. Because of the strong attachment of the aminophenyl groups, the regeneration of an electrochemically clean glassy carbon electrode required a mechanical polishing of the surface. The amine groups were grafted on the carbon surface directly by polishing the electrode with $3 \mu\text{m}$ aluminum oxide powder to which 1 M ammonia solution was added [17]. The NHS ester of electroactive dinuclear iron complex [18] was allowed to react for seven days in dichloromethane with GC electrodes either modified with aminophenyl groups or freshly polished in the presence of ammonia (Scheme 1, step (b)). The electrode was then rinsed, sonicated in MeCN and finally transferred into an electrochemical cell containing only MeCN + Bu₄NPF₆. Cyclic voltammograms were recorded between 0 and $-2.5 \text{ V vs. Ag/Ag}^+$ at scan rates ranging from 0.02 to 5.0 V s^{-1} .

3. Results and discussion

The voltammograms of an aminophenyl-modified electrode reacted with the diiron complex exhibit a chemically reversible reduction wave at $E_{1/2} = -1.95 \text{ V vs. Ag/Ag}^+$ (Fig. 1), a potential close to that of the reversible reduction of $[\text{Fe}_2(\text{SCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{S})(\text{CO})_6]$ in solution [10]. This wave is ascribed to the reduction of the diiron complex because the aminophenyl group is not electrochemically active in this potential region (see Experimental, [16]). At a scan rate of 0.5 V s^{-1} , the peak to peak separation (ΔE_p) is 0.17 V , a value significantly larger than the value expected for an idealized monolayer displaying a Nernstian charge transfer [19]. Large ΔE_p values are not uncommon as Savéant and

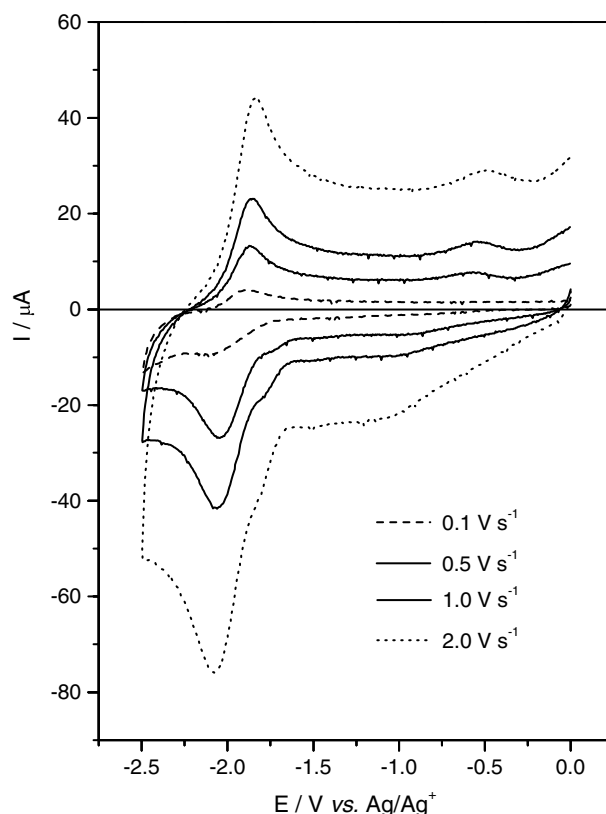
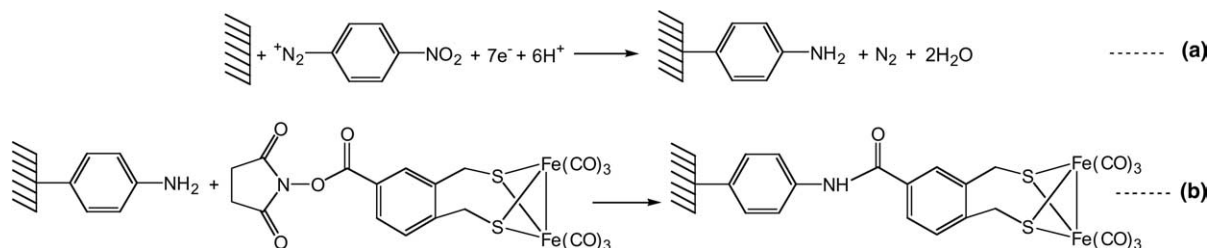


Fig. 1. Cyclic voltammograms in MeCN + Bu₄NPF₆ of the aminophenyl-modified GC electrode grafted with the diiron complex. Electrode surface area: 0.071 cm^2 .



Scheme 1. Two-step procedure for grafting the diiron complex on the GC surface.

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