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Ferrocene-Nafion Modified Electrode And Its Catalysis For Cerium (IV)

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Summary: Ferrocene-Nafion modified electrode is prepared, it exhibits an interesting electrocatalysis for Ce(IV) reaction.

Many investigations have been done on ferrocene (Fc) derivative and polymer modified electrodes,[1-6] but seldom reported the modified electrodes simply with Fc containing no substituents. Because in the latter case it was very difficult to attach the modifier to the electrode surface by conventional methods such as plasma polymerization,[1] electrodeposit,[2] electropolymerization,[3] covalence link,[4] ion exchange[5] and polymer coating[6] etc. Nafion modified electrodes[7-10] have attracted much interest for its ion exchange property. Considering Nafion possesses another property-hydrophobic interaction, here we propose a noval modified electrode with complex Fc by the help of Nafion. The Fc-Nafion modified electrode prepared shows well defined cyclic voltammogram of Fc. It has more stable and reversible voltammetric characteristics compared with other Fc derivative electrodes. What interesting characteristics of this Fc-Nafion modified electrode is, we find a catalytic phenomenon for cerium (IV).

EXPERIMENTAL

Reagents

Ferrocene and its derivatives, such as α-hydroxyethyl ferrocene (HEFc), 1,1′-bisα-hydroxyethyl ferrocene (BHEFc), acetoferrocene (AFc), 1,1′-bis-acetoferrocene (BAFc) and vinylferrocene (VFc) were home made. Diluted 5 wt% Nafion (Aldrich Co. U.S.A.) to 1 wt% with solution of 90% ethanol and 10% water. Ammonium ceric sulphate and other reagents were of analytical grade. All Fc and its derivatives were prepared by using acetonitril except that of vinylferrocene by dichloromethane. Electrolyte solution used was 0.5 M H_2SO_4, stock solution of cerium (IV) and H_2O_2 were prepared by 0.5 M H_2SO_4, but for ascorbic acid by a solution of 0.0018 M H_2SO_4 + 0.2 M K_2SO_4.

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Electrode and apparatus

A three-electrode cell was employed, which had a saturated calomel electrode (SCE) with double salt bridges as reference electrode, a platinum wire as auxiliary electrode and the modified glassy carbon (GC) electrode as working electrode. Electrochemical experiments were performed on a RDE model 4 potentiostat/galvanostat (Pine Instrument Co.) and a BAS model CV-47 voltammograph (BAS Inc. USA). All experiments were conducted at room temperature. Preparation of Fc-Nafion CME: GC electrode was polished with 0.5 um α-Al_2O_3 powder, washed and sonicated with water and ethanol, then dried. A mixed ethanol solution of Nafion 5–10 ul (1 wt%) and Fc 5–10 ul (0.01–0.08 M) was diped on GC electrode surface, after drying a tightly attached coating is formed, based on the hydrophobic interaction between Fc and Nafion, so a Fc-Nafion modified electrode was prepared.

RESULTS AND DISCUSSION

Voltammetric behavior of Fc-Nafion modified electrode

Figure 1 shows the cyclic voltammograms of newly prepared Fc-Nafion CME immersed in electrolyte solution during potential scanning between 0.6V and -0.2V. At the beginning, its wave is sluggish and small, subsequently, the currents rise up with potential scans until a distinct redox couple of Fc appears, then to a steady state after a few minutes. This process can be considered as Fc becomes ferricinium with the potential towards to positive, meanwhile the Na^+ ions at sulphonate group of Nafion enter in electrolyte solution and/or the anions in electrolyte solution dope in the Fc-Nafion film, which results in increasing the conductivity of both electrons and ions. Steady state of the Fc redox couple could be rapidly attained under potential step to $+0.5$ V only after a few seconds. In Figure 2 are illustrated the cyclic voltammograms that were obtained in electrolyte solution with steady state of Fc-Nafion modified electrode at different scan rate. The voltammetric characteristics of Fc-Nafion modified electrode in aqueous solution are as follows: $i_{pa} = i_{pc}$, $\Delta E_p = 60$ mV (scan rate $\upsilon = 10$ mV/s), $E_{1/2}$ (vs. SCE) $= 0.15$V. $E_{1/2}$ is approximately constant with υ, ΔE_p increases slightly with increasing υ due to the resistance of the Nafion film, i_{pa} and i_{pc} are proportional to $\upsilon^{1/2}$, so the electrode reaction in the film is a diffusion-controlled redox process. Surface coverage (Γ) of electroactive Fc groups on the surface from 5 ul Nafion and 5 ul 0.08 M Fc solution is estimated according to an area under cyclic voltammogram at $\upsilon =$ 100mV/s is ca. 1.38×10^{-8} mol/cm^2. Based on density of Nafion[11] and slope of $i_p - \upsilon^{1/2}$ curve, the apparent diffusion coefficient is estimated as 2.5×10^{-9} cm^2/s.

Compared with other Fc derivative modified electrodes[1-6] Fc-Nafion electrode shows more reversible electrochemical redox reaction, this may be because hydrophilic property of SO_3^- groups on Nafion improve the redox activity of the electrode in aqueous electrolyte solution. Moreover, the electrode has good stability, i_p is constant after being immersed or scanned in aqueous electrolyte solution over several hours and dried in air.

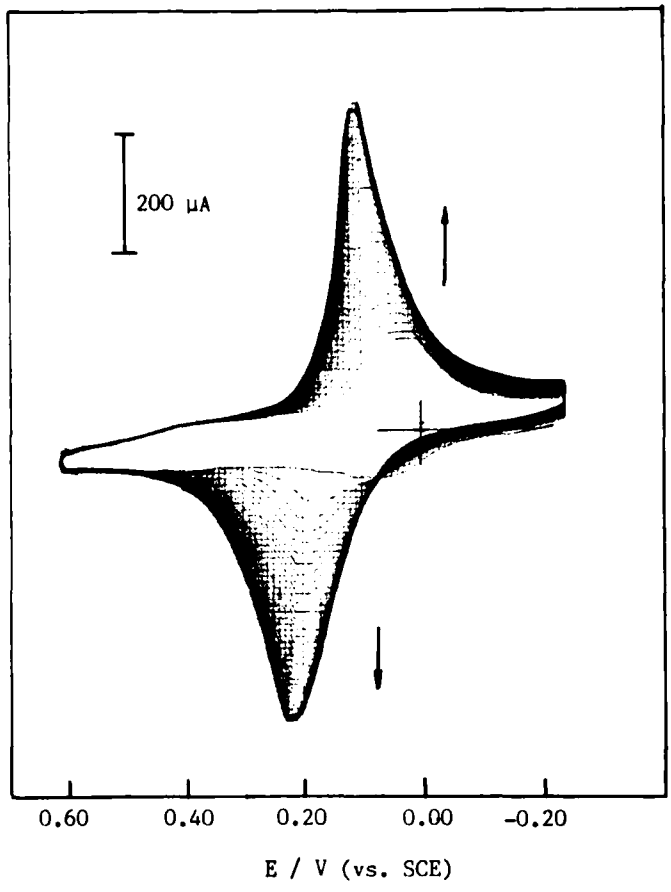

FIGURE 1 Cyclic voltammograms of newly prepared Fc-Nafion modified electrode immersed in 0.5 M H_2SO_4 during potential scans. Coating film: 10 μl Nafion (5 wt%) + 10 μl 0.08 M Fc. Potential range: from 0.6V to −0.2V. Scan rate: 100mV/s.

Catalytic phenomenon of cerium by Fc-Nafion modified electrode

It is known that cerium (IV) is a strong oxidizing agent with high redox potential aqueous solutions. The electrode reaction of cerium (IV) at various electrodes are quite irreversible. In our experiment, cerium (IV) in acidic aqueous solution is electroinactive on bare GC electrode over potential range 0.0–0.7V, no redox reaction takes place. Interestingly, we find that when GC electrode is coated with a mixture of Fc and Nafion and immersed in 0.5 M H_2SO_4 solution containing cerium (IV), a distinct redox could appear near the potential of Fc in the Fc-Nafion film, as shown in Figure 3. The i_p increases evidently, peak-peak separation decreases, peak shapes are steeper compared with that in blank solution (0.5 M H_2SO_4). Obviously, this phenomenon is related with cerium (IV) in solution and that cerium (IV) may involve in the electrode process, so it is investigated further with dynamic method—rotating disc modified electrode. The experiments reveal

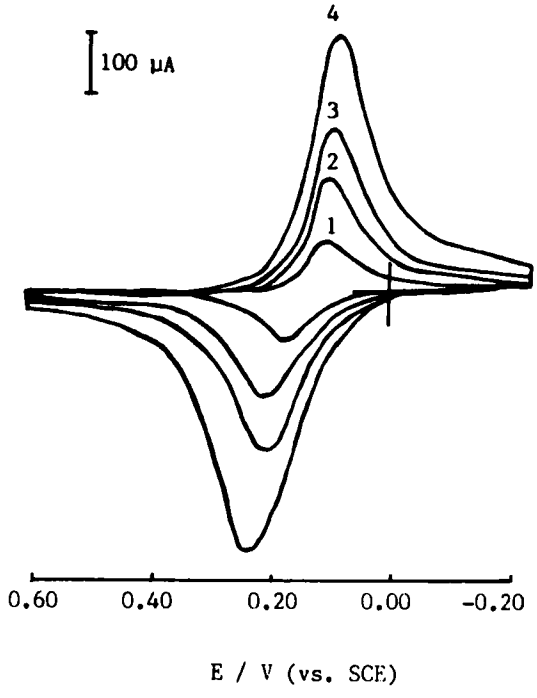

FIGURE 2 Cyclic voltammograms of Fc-Nafion modified electrode reached steady state with scan rate: curve 1, 2, 3 and 4 corresponds to υ = 10, 30, 50 and 100 mV/s respectively. Other conditions are the same as in Figure 1.

that the modified electrode in cerium (IV) solution is difficult to yield a limiting current (i_l) at low rotating rate, only exhibits a limiting current when rotating rate is high enough (above hundreds rpm). But when rotating rate is increased further, i_l is no longer increased, it means that cerium (IV) does participate electrode reaction, Fc attached on the GC electrode surface may catalyze cerium (IV) reaction, rate controlling process is surface electrode process rather than mass transfer one. It should be noted that neither electrode coated only with Nafion nor coated only with Fc can make this catalysis. This indicates that both the domain structure of Nafion polymer and the attached Fc property confining together induce such an interesting catalysis for cerium (IV), the latter may enter the hydrophilic domain of the film by ion exchange of Nafion, following reaction may take place:

$$Fc + Ce(IV) \longrightarrow Fc^+ + Ce(III) \qquad C$$

$$Fc \longrightarrow Fc^+ + e \qquad E$$

Oxidation (at the same time)

$$Fc^+ + Ce(III) \longrightarrow Fc + Ce(IV) \qquad C$$

$$Fc^+ + e \longrightarrow Fc \qquad E$$

Reduction (at the same time)

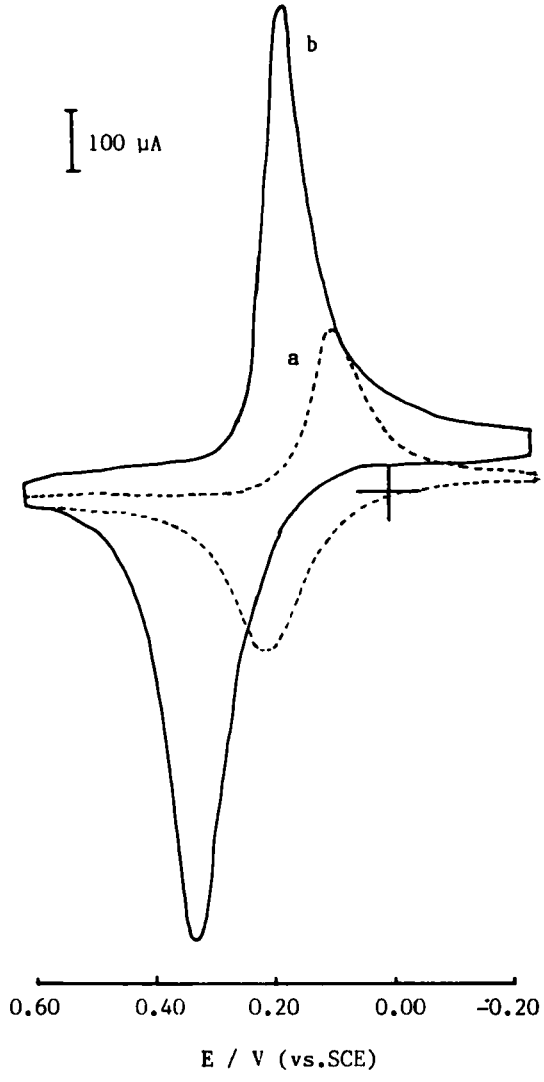

FIGURE 3 Catalytic wave of Fc-Nafion modified electrode to cerium (IV) in solution: (a) blank solution; (b) 10 mM cerium (IV). Scan rate: 50 mV/s. Other conditions are the same as in Figure 1.

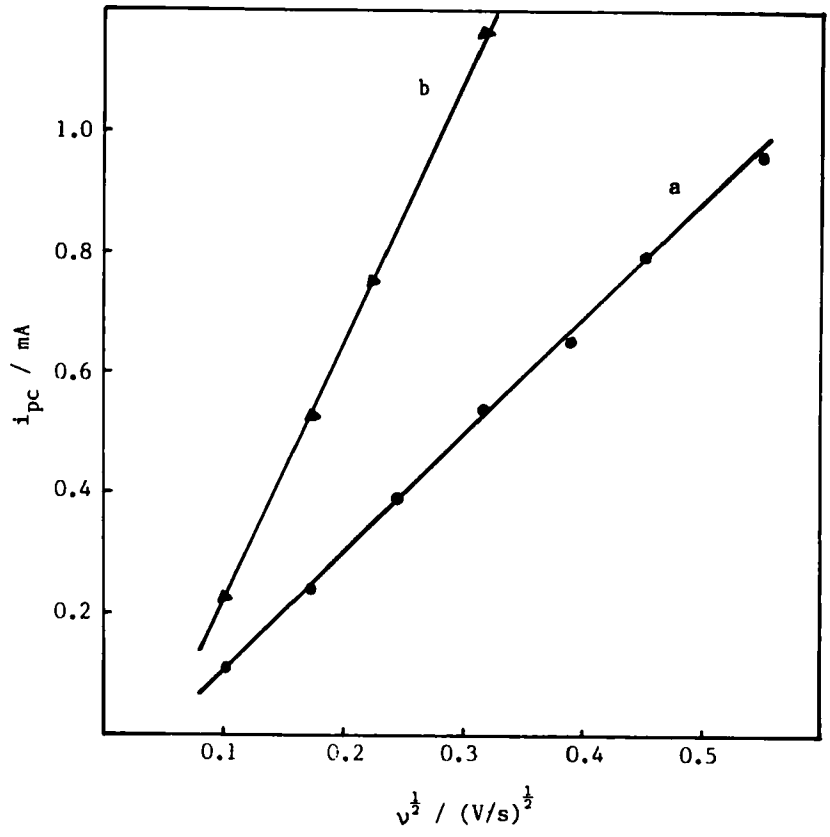

FIGURE 4 A plot of peak current vs. scan rate at Fc-Nafion modified electrode: (a) blank solution; (b) 10 mM cerium (IV).

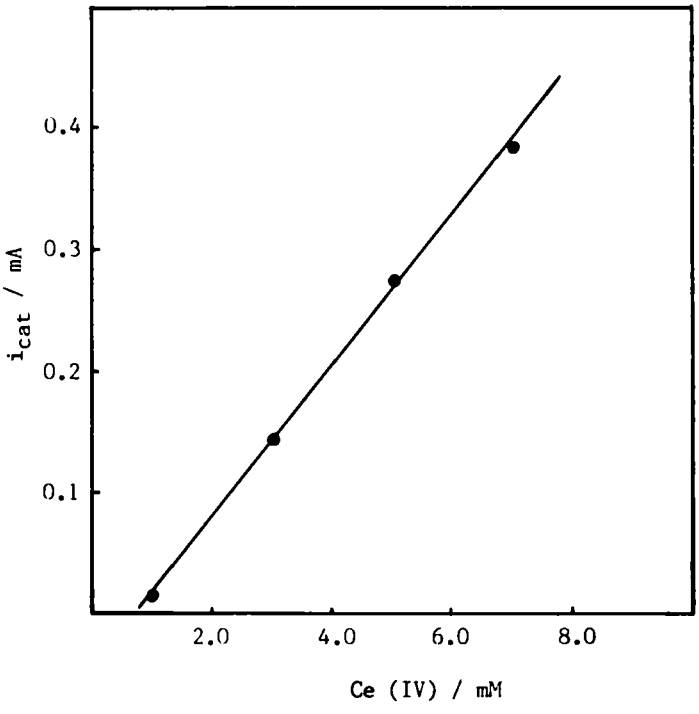

FIGURE 5 Relationship of catalytic current with cerium (IV) concentration at Fc-Nafion modified electrode.

The catalytic current (i_p) is linear with $v^{1/2}$ at different scan rates (see Figure 4), but the slope is larger than that of blank solution. Figure 5 shows that i_p is proportional to cerium (IV) concentrations in solution, this suggests a possible application for cerium (IV) analysis. But stability of the modified electrode immersed in cerium (IV) solution is not as good as in blank solution, i_p drops after a longer immersing time, perhaps due to oxidisability of cerium (IV) to deteriorate the film.

It is quite strange that modified electrode with Fc derivative containing a substituent, such as HEFc, BHEFc, AFc, BAFc and/or VFc etc., show no apparent catalysis for cerium (IV).

Fc-Nafion modified electrode has selectivity for catalysis to certain species not only based on Fc but also owing to the exit of Nafion as well. It can also catalyze reduction of neutral molecule H_2O_2 besides cation cerium (IV) (Figure 6), but can't do anion ascorboc acid, while the latter can usually be electrochemically catalyzed by Fc derivatives coated electrodes.[1b,6] This is another feature of this modified electrode different from others. The mechanism of the catalysis is under study.

Acknowledgment

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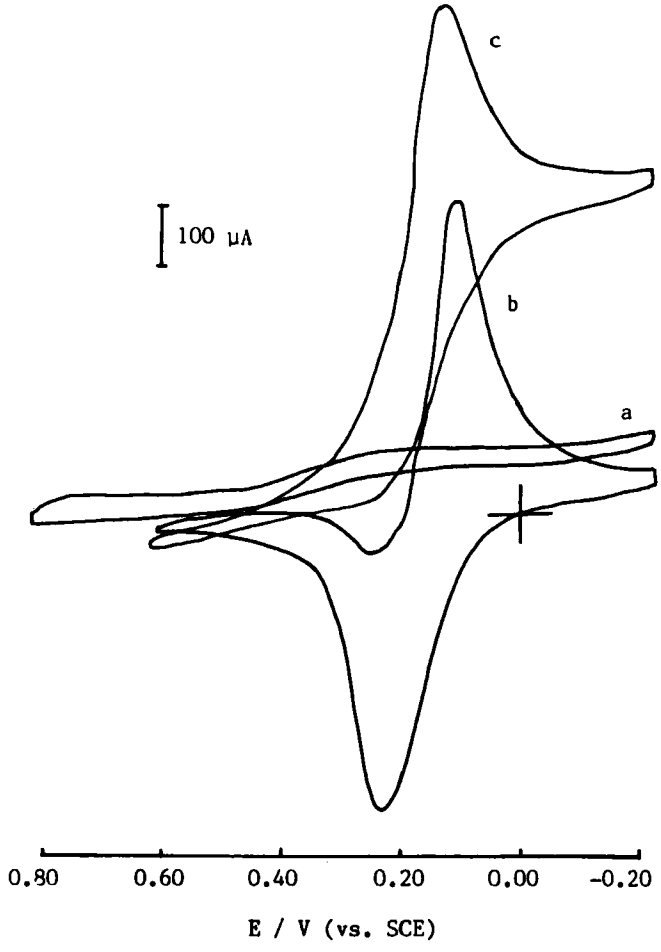

FIGURE 6 Catalytic wave of Fc-Nafion modified electrode to H_2O_2 in 0.5 M H_2SO_4 solution. (a) bare GC electrode in 0.098 M H_2O_2 solution; (b) Fc-Nafion modified electrode in blank solution; (c) Fc-Nafion modified electrode in 0.098 M H_2O_2 solution. Scan rate: 100mV/s.

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