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Application of the SPE Method to Organic Electrochemistry. VIII. The Incorporation of an Iron Redox Couple into Pt-Nafion and Its Behavior as a Mediator

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Fe^{2+} and Fe^{3+} were incorporated into Pt-Nafion. The full incorporation of Fe^{2+} into H^+-type Nafion was attained beyond 0.3 M† $FeSO_4$. The ion-exchange selectivity of Fe^{2+} was estimated to about 2 to H^+. The incorporated ions exhibited diffusional behavior inside the composite electrode. The formal potential of the incorporated iron(III/II) redox couple was dependent on both the H_2SO_4 and the Fe^{3+} and Fe^{2+} concentrations. The potential shift was, however, not so large as that reported on some redox systems on polymer-coated electrodes. The incorporated redox couple was revealed to behave as a mediator in the oxidation of L-ascorbic acid.

The present authors have investigated the application of the SPE method to organic electrochemistry[1,2] using Nafion as an SPE material. Electroorganic syntheses mediated by a redox system are very attractive and have been investigated by many workers. The present authors also attempted to utilize some redox mediators in an SPE electrolyzer, though only mediators dissolved in a solution were used.[3,4] The fixing of a mediator system into an SPE composite electrode would facilitate the separation process after an electrolysis and would demand only a small amount of the mediator. These advantages enable one to use an expensive mediator. In this work, the use of a redox mediator fixed in an SPE composite electrode prepared by the electroless deposition of Pt on Nafion (Pt-Nafion) was preliminarily examined using an iron-redox system.

Pt-Nafion has inherently the structure of a Nafion-coated electrode. Many workers have investigated Nafion-coated electrodes prepared by the casting of a Nafion solution.[5,6] A solution-cast Nafion film does not, however, have the well-known structure of Nafion without curing above 120 °C.[7] On the other hand, nobody would hesitate to accept the reported structure model of Nafion on Pt-Nafion prepared by the electroless plating method under the mild conditions adopted in this work. Pt-Nafion, therefore, may serve as a typical model of an electrode coated with Nafion with a better defined structure. The electrochemical behavior of an iron-redox couple in Pt-Nafion will also be briefly examined.

Experimental

Chemicals. Commercially available chemicals of a reagent grade were used without further purification.

Pt-Nafion Composite Electrodes. Nafion 125, a perfluorinated cation-exchange membrane, was used as an SPE material. Platinum was deposited on one side of the Nafion from chloroplatinic(VI) acid employing an electroless plating method described peviously,[8] using $NaBH_4$ as a reductant. After electroless plating, platinum was further electrolytically deposited in order to decrease the surface ohmic resistivity to less than 0.7 Ω between the two ends of the deposit (3 cm in diameter).

Electrolysis Cell. The SPE composite electrode, with an effective geometric surface area of 3.1 cm^2, was placed in a glass cell described elsewhere.[2] The electrode potential was set vs. the Ag/AgCl reference electrode via a Luggin capillary inserted in a counter-electrode compartment using a potentiostat (Hokuto Denko HA-301). During experiments, argon was introduced into the working-electrode compartment. In all cases, the set potential contained a junction potential at the interface between Nafion and the contacting solution and a fairly large ohmic drop through the Nafion.

Incorporation of Fe^{2+} and Fe^{3+} into Pt-Nafion. After platinum deposition, the Pt-Nafion was immersed in 1M H_2SO_4 for more than 2h in order to change the counter ion into H^+. This H^+-type Pt-Nafion was then immersed in a $FeSO_4$ or $Fe_2(SO_4)_3$ solution of different concentrations under argon purging into the solution.

Amounts of Fe^{3+} and Fe^{2+} Incorporated in Pt-Nafion. A chronoamperometry technique was first used to measure the amount of iron ions in the Pt-Nafion. The decaying current after potential stepping with and without incorporation was integrated. The difference in values with and without the incorporation gave the amount of Fe^{2+} or Fe^{3+} in Pt-Nafion.

Pt-Nafion incorporated with Fe^{2+} or Fe^{3+} was immersed in 2M H_2SO_4 or 0.3M EDTA so that the incorporated Fe^{2+} or Fe^{3+} could be extracted into the solution. The amount of iron ions in the extract was measured by a fluorescent X-ray analysis method using Kelex Ultra-Trace 0600. In some experiments, iron(II) or iron(III) ion was oxidized by H_2O_2 or reduced by L-ascorbic acid[AH_2] respectively during immersion in order to fix the ionic form at Fe^{3+} or Fe^{2+}.

Mediation by Iron-Redox Couple Incorporated in Pt-Nafion. Using a 25 mM AH_2 aqueous solution, the capability of mediation by the iron-redox couple was examined by means of the cyclic voltammetry and potential pulse electrolysis techniques. An AH_2 solution was introduced into either the working or counter-electrode compartment.

Results and Discussion

The Incorporation of Iron Ions into Pt-Nafion. The amounts of Fe^{2+} incorporated into Pt-Nafion from aqueous $FeSO_4$ in various concentrations were

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† 1M=1 mol dm^{-3}.

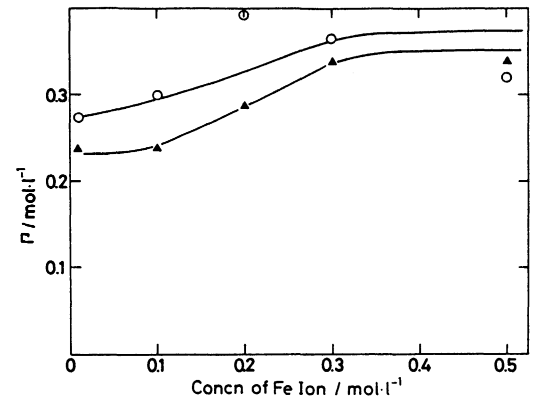


Fig. 1. The amount of Fe^{2+} up-taken into Nafion 125, Γ, by X-ray fluorescence (○) and chronoamperometric (▲) measurements.

measured by means of a chronoamperometry technique and fluorescent X-ray analysis. The incorporated Fe^{3+}/Fe^{2+} showed diffusional behavior, which allowed us to use a chronoamperometry technique in order to estimate the amount of Fe^{2+} in Pt-Nafion. As Fig. 1 shows, the results obtained by the two methods agreed fairly well. The amount reached the ceiling value of about 0.34—0.37 mol dm^{-3}-whole wet resin in a 0.30 M $FeSO_4$ soaking solution. The exchange site concentration of Nafion 125 after standard boiling-water treatment in the H^+ form was estimated as ca. 1 equivalent dm^{-3}-whole wet resin, ca. 3 equivalent dm^{-3}-dry resin. The results obtained here correspond to ca. 0.7 equivalent dm^{-3}-whole wet resin, which is about 70% of the estimated value of a full exchange.

Redox Behavior of Incorporated Fe^{3+} and Fe^{2+} Ions. Incorporated iron ions showed redox behavior on cyclic voltammetry measurements. After a decrease in the current during several initial sweeps, steady voltammograms were obtained. Changing a potential sweep rate, the peak currents were examined on Pt-Nafion placed in contact with 0.025 M H_2SO_4, which had precedingly been equilibrated with 0.25 M $Fe_2(SO_4)_3$. The anodic and cathodic peak currents exhibited a linear dependence on the square root of the sweep rate, suggesting the usual diffusional properties of the redox species existing in the Pt-Nafion and a negligible contribution from a migration effect. On the other hand, a linear dependence of the peak currents on the sweep rate has been reported on many polymer-coated electrodes, including a Nafion coated electrode, and an electron-hopping conduction process has been reported to take place in a Nafion-coating film on electrodes.[6,10] In the present case, however, we need not consider this process, because the Nafion keeps its structure as an ion-exchange membrane in which the conduction is exclusively sustained by the diffusional and migrational movements of ionic species, and so electronic conduction must be insignificant.

The Exchange Selectivity of Fe^{2+}. The increase in the H_2SO_4 concentration at 0.05 M $FeSO_4$ caused a decrease in the anodic peak current on Pt-Nafion incorporated with iron ions. This decrease implies the exchange of H^+ with Fe^{2+} or Fe^{3+} in Pt-Nafion. The exchange selectivity, K, of ion exchange membranes was calculated. Assuming the activity coefficient of Fe^{2+} $\gamma_{Fe}=1$ and using a mean activity coefficient of H_2SO_4 for γ_H, the molar fraction of Fe^{2+} in Pt-Nafion, $\bar{x}$, was calculated. $\bar{x}$ is shown in Fig. 2. Since the $\bar{x}$ calculated assuming $K=2.0$ agrees well with the experimental results, we obtained the selectivity constant of 2.0 for Fe^{2+} in Nafion. The value of $K=2.0$ is acceptable in view of the reported values of 0.97, 1.24, 3.60, and 2.30 for Zn^{2+}, Co^{2+}, Cu^{2+}, and Mg^{2+} respectively.[11]

Formal Potential of the Iron-Redox Couple Incorporated in Pt-Nafion. The formal potential of the iron-redox couple incorporated in Pt-Nafion, $E_p{}^f$, was obtained by means of cyclic voltammetry measure-

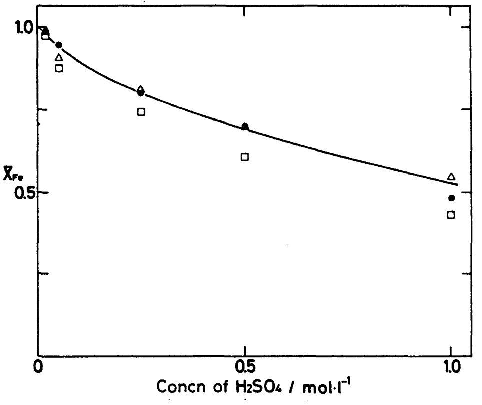


Fig. 2. The dependence of Fe^{2+} molar fraction inside Pt-Nafion, $\bar{x}$, on H_2SO_4 concentration at 0.05 M $FeSO_4$. Solid line; experimental result, Calculated values assuming $K=2.0$ (△) and $K=1.4$ (□).

Table 1. Dependences of the Formal Potential, E^f, on the H_2SO_4 Concentration at 0.05 M $FeSO_4$ on Pt-Nafion and Pt Plate Electrodes

H_2SO_4/M	E^f/mV Pt-Nafion	E^f/mV Pt-plate	ΔE^f/mV
0.005	446	465	−14
0.025	462	468	−6
0.05	460	465	−5
0.25	468	465	+3
0.5	467	461	+6
1.0	486	466	+20

Table 2. Dependences of the Formal Potential, E^f, on the $FeSO_4$ Concentration at 0.025 M H_2SO_4 on Pt-Nafion and Pt Plate Electrodes

$FeSO_4$/M	E^f/mV Pt-Nafion	E^f/mV Pt-plate	ΔE^f/mV
0.005	430	466	−36
0.01	435	464	−29
0.05	453	456	−3
0.1	463	456	+3
0.3	470	450	+20

ments; a set of values are listed in Tables 1 and 2, together with the values in an aqueous solution on a conventional bare Pt electrode, E_s^f. The values were calculated as a middle point between the anodic and cathodic peak potentials. As shown in the tables, the potential difference, $\Delta E^f = E_p^f - E_s^f$, changes from a negative to a positive value with an increase in the H_2SO_4 or Fe_2SO_4 concentration. Some authors have previously noticed a systematic shift of the formal potential of some redox couples incorporated in the polymer coating on electrodes. Braun et al.,[12] for instance, reported a very big potential shift of $[Fe(CN)_6]^{3-/4-}$ (over 200 mV) incorporated in an anion-exchange layer on glassy carbon. Tsou and Anson[13] examined the shift of the formal potential of some redox couples using pyrolytic graphite electrodes covered with Nafion or a polymerized perfluorinated calboxylic acid type cation exchanger. They observed a negative ΔE^f for the more hydrophobic redox couples, $[Ru(NH_3)_6]^{3+/2+}$ and positive ΔE^f for the more hydrophobic redox couple, $[Os(bpy)_3]^{3+/2+}$. They explained this as follows. In the case of hydrophilic redox couples, the oxidized redox half is stabilized more by the electrostatic interaction with a coating polyelectrolyte than is the reduced redox half. In the case of hydrophobic redox couples, on the other hand, the reduced redox half is stabilized more by the hydrophobic interaction with the coating polyelectrolyte than is the oxidized redox half. They also explained the dependence of the potential shift on the ionic strength as the result of a combination of two interactions in the opposite direction, increased electrostatic interactions at a lower ionic strength, and stronger hydrophobic interactions at a higher ionic strength.

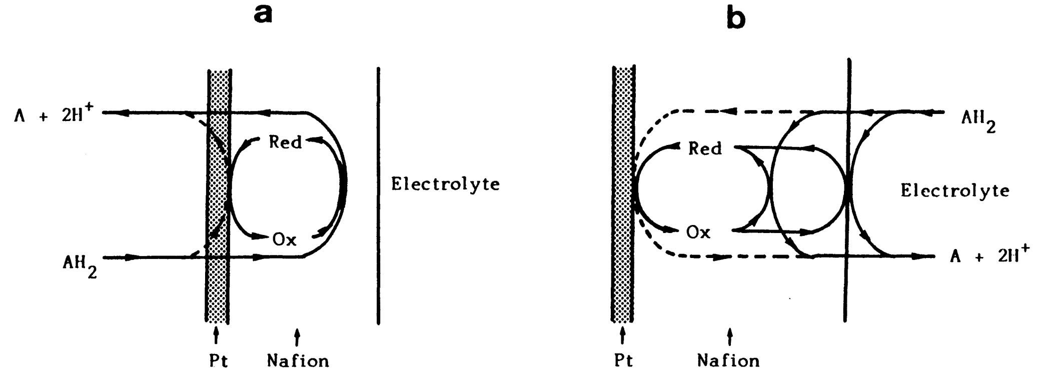
In the present results shown in Tables 1 and 2, however, neither the potential shift nor the change in ΔE^f with the concentration of the outer solution were so large as the value observed by Tsou and Anson. Iron(III) and iron(II) ions are so hydrophilic that the contribution of the hydrophobic interaction with Nafion is insignificant. The change in E^f with the concentration could be ascribed to the change in the Donnan potential, which was not estimated here. The characteristic ionomer structure of Nafion,[11] which is widely accepted, can be directly adopted in the case of Pt-Nafion, while the structure of Nafion on a polymer-coated electrode prepared from liquid Nafion should be dependent on the treatment after coating and might be different from the structure of the membrane Nafion. The ionomer structure of Nafion renders the behavior of the hydrophilic species inside the Nafion similar to that in the homogeneous aqueous phase. This leads to the smaller ΔE^f value on Pt-Nafion than on polymer-coated electrodes prepared from the liquid Nafion.

The redox potential of Fe(III)/Fe(II) is well-known to be affected by an anion in solution. In the present case, some direct effects of a $-SO_3^-$ group of Nafion, such as coordinating to and ion-pairing with redox cations, must be taken into consideration in any further discussion.

Indirect Oxidation of AH_2. From the above results, it seems that the redox potential of Fe(III)/Fe(II) in Nafion dose not differ much from the value in a usual aqueous system; the Fe(III) ion in Nafion can, therefore, be expected to oxidize AH_2 to dehydroascorbic acid.[14]

In the use of SPE composite electrodes incorporated with a redox mediator, two different configurations in the electrolysis system are possible, as is shown in Fig. 3. Case a is a distinguishing configuration for an SPE electrolyzer. In this case, a substrate solution is not required to contain any electrolyte; even neat substrate fluid can be used. Case b is the same configuration as in a usual polymer-coated electrode, though the coating polymer layer is much thicker than on the latter. In Case a, the substrate must be transferred to the reaction site through a thin, porous metal electrode layer. In Case b, the mediator or substrate must pass through a coating Nafion layer.

In the configuration of Case b, the electrode poten-



AH_2 : L-ascorbic acid, A : dehydroascorbic acid, Red : Fe^{2+}, Ox : Fe^{3+}

Fig. 3. Schematic diagrams of a mediation reaction by a redox couple incorporated in an SPE composite electrode. a: a substrate is introduced in a working electrode compartment, b: a substrate is introduced in a counter electrode compartment.

tial was stepped from 0.4 to 0.75 V, where the Fe(II) ion was oxidized to the Fe(III) ion. As is shown in Fig. 3 (b), AH_2 can be oxidized by two different courses: The direct oxidation of AH_2 on the Pt electrode bound to Nafion and indirect oxidation by the Fe(III) ion produced by the oxidation of the Fe(II) ion on the Pt electrode at the surface or inside the layer of the Nafion film. In the former, AH_2 has to penetrate through the Nafion layer and so reach the Pt electrode (the broken line in Fig. 3 (b)). In the latter, the Fe(III) ion has to move from the Pt electrode to the Nafion surface and so come in contact with the solution containing AH_2. If the Fe(III) ion meets with AH_2, which comes into the Nafion layer from the solution on the way to the Pt surface, it will oxidize the AH_2 there (the solid line in Fig. 3 (b)). The current due to the direct oxidation was estimated from measurements of the current after the potential stepping described above, without any incorporation of the iron-redox couple. Line a in Fig. 4 shows the direct oxidation current, the values of which increase linearly with the increase in the concentration of AH_2 in the counter-electrode compartment, as can be predicted from its simple diffusional mass-transfer through the Nafion layer. The incorporation of the iron-redox couple enhances the oxidation current after the potential stepping. The oxidation current should contain the oxidation of the Fe(II) ion incorporated in the Nafion layer. The latter would, however, fall off to zero after the consumption of the whole Fe(II) ion if Fe(II) was not regenerated by the reaction with AH_2. Therefore, the increase in the current should be ascribed to the indirect oxidation mediated by the iron redox couple, because the current was measured under steady-state conditions. The increase in current upon the incorporation of the iron-redox couple is shown by line b in Fig. 4. The increment was calculated by subtracting the values shown by line a from the values obtained with the incorporation. The subtraction does not give the correct value of the indirect oxidation in an exact sense, because the simple diffusional mass-transfer is no longer valid when diffusing AH_2 reacts with the Fe(III) ion on the way. However, the increment still gives evidence of the contribution of the indirect oxidation process. Details of the rate of the indirect oxidation relative to the direct oxidation will be discussed in successive papers, together with problems in the mass-transfer and reaction zone in the Nafion layer.

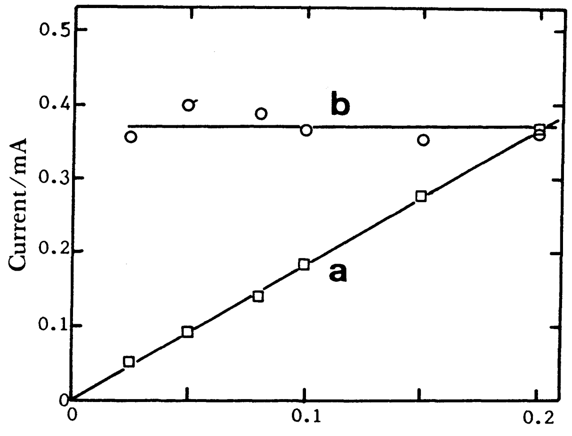


Fig. 4. Oxidation current of AH_2 in 25 mM H_2SO_4 in a counter electrode compartment of Pt–Nafion without incorporation of the redox couple (a), and with incorporation of Fe^{3+} and Fe^{2+} after subtraction of the direct oxidation current of AH_2 (b).

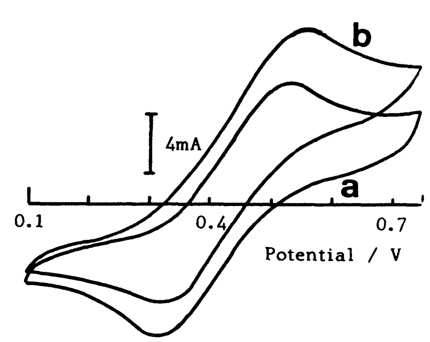


Fig. 5. Cyclic voltammograms on Pt–Nafion incorporated with Fe^{3+} and Fe^{2+} containing with water (a), and 25 mM AH_2 (b) in a working electrode compartment.

Figure 5 shows cyclic voltammograms obtained in the configuration of Case a in Fig. 3. Curves a and b were obtained without and with 25 mM AH_2 respectively in the working-electrode compartment. The current increases to the positive direction throughout the potential range of the potential sweep. It has been reported that AH_2 is oxidized directly at the potential examined here in the low pH region.[14] Therefore, it seems that the increase observed here was caused by both the direct oxidation of AH_2 on Pt and its indirect oxidation mediated by the iron-redox couple. The increase is more remarkable at the positive potential, where the Fe(II) ion is oxidized to the Fe(III) ion, than at the negative potential where the Fe(II) ion is stable. These phenomena suggest qualitatively that the indirect oxidation process takes place in the configuration of a in Fig.3. It is difficult to separate the contributions to the current-increase from the two courses of oxidation in this configuration. The increase in the current upon a mediatory action of the redox couple was, however, larger in the configuration of Case a than in that of Case b (cf. Fig. 3. This means that the former configuration is preferable. The results in Figs. 4 and 5 show the applicability of the redox couples incorporated in an SPE composite electrode as mediators for the electrochemical reactions of organic substances.

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