December, 1988] © *1988 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 61, 4183—4187 (1988)* 4183

Application of the SPE Method to Organic Electrochemistry. IX. Reaction Profiles of an Iron Redox Couple Incorporated into Pt–Nafion with Ascorbic Acid

Zempachi OGUMI,* Toshiyuki MIZOE, and Zen-ichiro TAKEHARA
Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto 606
(Received March 16, 1988)

Fe^{3+} has been incorporated into Pt–Nafion. The behavior of Fe^{3+} as a mediator was examined in detail in a system comprising the oxidation of L-ascorbic acid (AA) to dehydroascorbic acid (AD). The diffusion of AA in Nafion is slower than that of Fe^{3+}. The concentration profiles of Fe^{3+} and AA in Pt–Nafion have been clarified and a reaction of the mediator with AA took place within a very narrow zone close to the surface. The averaged diffusion coefficients of Fe^{3+} and AA are 1.5×10^{-7} cm^2 s^{-1} and 4.7×10^{-8} cm^2 s^{-1}, respectively.

The present authors have investigated the application of the SPE method to organic electrochemistry[1,2] using Nafion as an SPE material. The use of a mediator system in electroorganic syntheses gives some advantages, such as a higher reaction selectivity, easier separation, higher reactivity etc. It was clarified in a previous paper[3] by the present authors that an iron redox couple incorporated into Pt–Nafion acted as a mediator for the oxidation of L-ascorbic acid, AA, to dehydroascorbic acid, AD. In this work, the reaction of Fe^{3+} with AA and their concentration profiles in Pt–Nafion were both examined in detail.

Two configurations are possible in the use of SPE composite electrodes, as described in a previous paper.[3] In configuration a, in Fig. 3 in Ref. 3, substrates are introduced into the working electrode compartment. In configuration b of the same figure, substrates are introduced into the counter electrode compartment. The former configuration is more useful for enhancing the reaction rate. On the other hand, it is easier in the latter configuration to investigate concentration profiles in a composite electrode, since the contribution from any direct electrode reaction of the substrates is suppressed. The latter configuration (b) is focused upon here.

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,[4–6] owing to their potential applications to such electrochemical devices as sensors and electrochromic displays. The concentration profiles on polymer-coated-electrodes have been extensively investigated by Saveant and co-workers[7,8] as well as others. Polymer-coated electrodes were mainly prepared by using a solution casting method including Nafion-coating. Solution-cast films are thin and it is not easy to characterize their structure well. In some cases, the structure of a solution-cast film is different from that of a thicker membrane prepared by a conventional method. For example, a Nafion film cast from its solution, without an adequate following curing treatment, is different from the characteristic ionomer structure of Nafion. In the case of Pt–Nafion, the coating layer is thick (100—300 μm) and its structure is well characterized.[9] Utilizing these advantages, concentration profiles and a reaction zone inside the Nafion which coated a porous Pt electrode were investigated. The obtained results present a clearer typical model of the concentration distribution on Nafion-coated electrodes. These are useful in giving higher functions to SPE composite electrodes regarding their applications to organic electrochemistry.

Experimental

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

Pt–Nafion Composite Electrodes. Nafion 125 and Nafion 120 were used as SPE materials. These two Nafions are different only in their thickness, and are nominally 125 and 250 μm (5 and 10 mil) thick. After standard boiling water treatments, platinum was deposited on one side of the Nafion by a method previously described.[3] An iron redox couple was incorporated into Pt–Nafion by a previously described method.[3]

Electrolysis Cell. The electrolysis cell was composed of two compartments, a working electrode compartment (w.e.c. 15 cm^3) and a counter electrode compartment (c.e.c. 14.5 cm^3), which were divided by Pt–Nafion. Argon was filled in w.e.c. and an aqueous sulfuric acid solution (in most cases 0.025 mol dm^{-3}) without or with AA (in most cases 0.15 mol dm^{-3}) in c.e.c. The cell was thermostated at 25 °C.

Electrochemical Measurements. Chronopotentiometry, chronoamperometry, and steady state current measurements were adopted in order to obtain information on the concentration profiles of Fe^{3+} and AA. The apparent effective surface area of composite electrodes was 3.1 cm^2.

Results

The Concentration of Fe^{3+} inside Pt–Nafion. By a method similar to that used before,[3] the exchange selectivity of Nafion for Fe^{3+} was investigated. The concentration of Fe^{3+} in Pt–Nafion equilibrated with an Fe^{3+}solution of concentration higher than 0.3 mol dm^{-3} was 0.31 mol dm^{-3}-whole-wet-resin. Fe^{3+} is exchanged with other cations in the solution when it is soaked in an electrolyte solution free from Fe^{3+} until the concentration distribution reaches an equilibrium state between the contacting solution and Pt–Nafion. Therefore, after the electrolytic cell was set up and filled with a sulfuric acid solution in c.e.c. (14.5 cm^3), the concentration of Fe^{3+} inside Pt-Nafion decreased to 0.29 and 0.12 mol dm^{-3}-whole-wet-resin (Nafion 125) for 0.050 and 0.10 mol dm^{-3} in c.e.c., respectively.

The Thickness of Pt-Nafion. Swelling changes the volume of Nafion, resulting in a change in its thickness. The degree of swelling is known to be dependent on its pretreatment conditions. After the standard boiling water treatment, the thickness of Nafion 125 and 120 was measured using a micrometer. The averaged values were 139 and 284 μm, respectively, which approximately agreed with values 143 and 289 μm calculated using an empirical equation[9] of swelling while assuming an isotropic expansion by swelling.

Diffusion of Fe^{3+}. Chronopotentiometry measurements gave $i\tau^{1/2}$ of 29.6 mA s$^{1/2}$ on Pt-Nafion containing Fe^{3+} and contacting with 0.05 mol dm^{-3} H_2SO_4. Substituting 0.29 mol dm^{-3} for the concentration of Fe^{3+}, the Sand equation,[10] Eq. 1, gave the diffusion coefficient of Fe^{3+} in Pt-Nafion, and $D_{Fe}=1.5\times10^{-7}$ cm^2 s^{-1} was obtained.

$$I\tau^{1/2}=nFAcD^{1/2}\pi^{1/2}/2 \qquad (1)$$

This value is reasonable, compared with the value for Na^+, $D_{Na}=9.44\times10^{-7}$ cm^2 s^{-1}, measured by a tracer method for Nafion 120.[11]

The constant current for a reduction of Fe^{3+} on Pt-Nafion contacting 0.5 mol dm^{-3} $Fe_2(SO_4)_3$ was measured under mass-transfer limiting conditions using Nafion 125 and Nafion 120 at 200 mV vs. Ag/AgCl. Assuming that the diffusion layer thickness is equal to the Nafion thickness (139 and 284 μm, respectively), a calculation using Eq. 2 and $c=0.31$ mol dm^{-3} gave $D_{Fe}=1.4\times10^{-7}$ cm^3 s^{-1}.

$$I=nFADc/d \qquad (2)$$

After equilibrating Fe-type Pt-Nafion with 0.05 mol dm^{-3} H_2SO_4, the electrode potential was stepped from 700 mV (vs. Ag/AgCl) to 200 mV, where Fe^{3+} was reduced to Fe^{2+} under mass-transfer limiting conditions. As plotted in Fig.1, in the range of small t the transient current decreased linearly with $t^{1/2}$, and in the range of larger t the current remained constant. Using the Cottrell Eq. 3,[12] and substituting $c=0.29$ mol dm^{-3}, $D_{Fe}=1.8\times10^{-7}$ cm^2 s^{-1} was obtained.

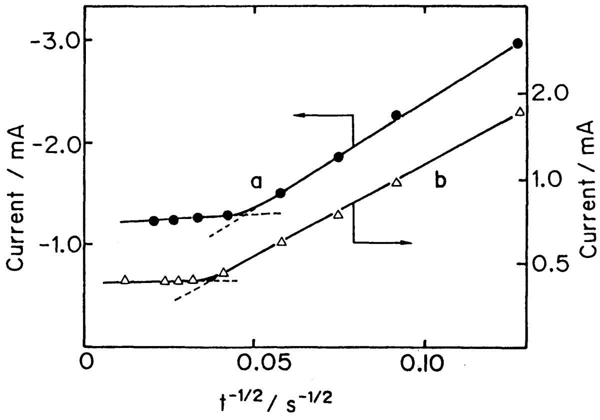

Fig. 1. Cottrell plots of the reduction of Fe^{3+} (a) and oxidation of L-ascorbic acid (b) on Pt-Nafion 125. Fe^{3+}: 0.75—0.20V, 0.2 M Fe^{3+} and 25 mM H_2SO_4 in c.e.c.
AA: 0.25—0.75V, 0.15 M AA, 25 mM H_2SO_4 in c.e.c.

$$I=nFAcD^{1/2}/\pi^{1/2}t^{1/2} \qquad (3)$$

The diffusion layer thickness increased with the time after the potential stepping; a model involving semiinfinite diffusion was no longer valid after the time that the surface of Nafion began to significantly affect the diffusion of Fe^{3+}. On the other hand, at a longer time, the reduction was controlled by the mass transfer, which was limited by the linear diffusion through the Nafion layer of Pt-Nafion under steady state conditions. This situation leads to a constant current as shown in the figure. The intersecting point of two linear lines gives the time when the thickness of the diffusion layer becomes equal to the thickness of the Nafion. Using $d=(\pi Dt)^{1/2}$ and $t^{-1/2}=0.05$ $s^{-1/2}$ (at the intersecting point), a calculation gave the thickness of 143 μm, which agreed fairly well with the directly measured value, 139 μm.

Diffusion of AA. Since AA is known to be oxidized on a Pt electrode, the diffusion coefficient of AA in Pt-Nafion was measured by electrochemical methods. Chronoamperometry measurements were carried out by stepping a potential of Pt-Nafion without any incorporation of iron ions from 250 to 750 mV, at which all AA reaching the electrode surface on Pt-Nafion through the Nafion layer was sufficiently quickly oxidized to dehydroascorbic acid. As shown in Fig. 1, the transient current decreased proportionally to $t^{-1/2}$ for a shorter time. A slope of i-$t^{-1/2}$ gives the diffusion coefficient using the Cottrell equation, Eq. 3, if the concentration of AA inside the Pt-Nafion c_{At} is known. As discussed below, a concentration in a solution contacting Pt-Nafion can be adopted as the value in Pt-Nafion within an error of less than 10%. Under this situation, the Cottrell equation, Eq. 3, leads to the diffusion coefficient of AA in Pt-Nafion, $D_{AA}=4.4\times10^{-8}$ cm^2 s^{-1}. By a treatment similar to that in the chronopotentiometry of Fe^{3+}, the intersecting point of a Cottrell plot with a steady state current (which corresponds to the diffusion limiting current through the Nafion 125 layer on Pt-Nafion) gave a thickness of 127 μm. The value is about 10% less than the measured value for Nafion 125 (139 μm). The diffusion current of AA through the Nafion layer on Pt-Nafion at 750 mV was proportional to the concentration of AA in the contacting solution. The diffusion current using Nafion 125 was two-times larger than that with Nafion 120, as expected from the difference in the diffusion flux through two membranes of different thickness.

Discussion

The concentration profiles of AA and Fe^{3+} inside Pt-Nafion is discussed. The reaction of AA, with Fe^{3+}, in an aqueous solution is described as follows.[13]

$$-dc_{At}/dt = kc_{At}[Fe^{3+}] \tag{4}$$

c_{At}; total concentration of ascorbic acid AA dissociates to AA^- and AA^{2-} in an aqueous solution. Neglecting the second dissociation, AA^{2-} since it makes a very small contribution,[13] Eq. 4 can be rewritten

$$-dc_{At}/dt = k_1[AA^0][Fe^{3+}] + k_2[AA^-][Fe^{3+}]. \tag{5}$$

Using the dissociation constant, K_1,

$$-dc_{At}/dt = (k_1 + k_2K_1/[H^+])[AA^0][Fe^{3+}]. \tag{6}$$

The rate constants, k_1 and k_2, and the dissociation constant, K_1, were obtained previously:[13]

$$k_1 = 1.6\times10^2\ \mathrm{mol^{-1}\,dm^3\,s^{-1}},$$
$$k_2 = 6.4\times10^3\ \mathrm{mol^{-1}\,dm^3\,s^{-1}},$$

and

$$K_1 = 9.2\times10^{-5}\ \mathrm{mol\,dm^{-3}}.$$

Since Fe^{2+} is generated inside Pt-Nafion by a reaction of Fe^{3+} with AA, the cation is demanded in Nafion in order to satisfy the requirements of electroneutrality there. In this system, H^+ produced by the oxidation of AA satisfies this requirement. Further, as discussed previously, not all counter ions of Nafion are changed to Fe^{3+}, but some H^+ coexists in the Nafion as a counter ion. For these reasons, the concentration of H^+ at the reaction site in Pt-Nafion is higher than 0.29 mol dm^{-3} under the situation that the reaction between AA and Fe^{3+} takes place. This consideration allows one to neglect the second term in the parenthesis of Eq. 6, namely to neglect the contribution from the reaction of dissociated ascorbic acid. Equation 6 simplifies as follows:

$$-dc_{At}/dt = k_1[AA^0][Fe^{3+}]. \tag{7}$$

Assuming the simple model shown in Fig. 2, the concentration profiles of AA and Fe^{3+} were calculated using this equation. In this model it was assumed that a reaction is completed at the surface where AA and Fe^{3+} meet. Saveant and co-workers have extensively investigated the concentration profiles on polymer-coated electrodes.[7,8] The rate constants and diffusion coefficients of electroactive species and substrates through both a coating layer and a solution should be taken into consideration as factors which affect the concentration profiles in the coating layer. In the present treatment, the diffusion through a solution contacting Pt-Nafion is neglected because a much slower diffusion through the coating layer is expected. Yeager et al. investigated the mass transport of Na^+ through Nafion and through a depletion layer formed on the surface of Nafion.[14] Their result that the thickness of the depletion layer was as thin as 15 μm, supports the expectation that the mass transfer is predominantly controlled by the diffusion through Nafion. The reaction rate is also considered to be very fast, compared with the rate of mass transfer.

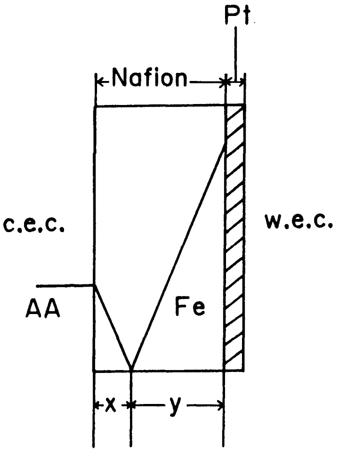

Fig. 2. A simplified model of the concentration profile of indirect oxidation of AA by Fe(3+/2+) redox couple inside the Pt-Nafion. x: diffusion layer thickness of AA,y: diffusion layer thickness of Fe^{3+}.

Some specific partition has been observed for many species at the interface between an ion-exchange membrane and the solution.[15] Therefore, the concentration of AA inside Pt-Nafion might be different from that in the solution. As discussed above, all ascorbic acid exists in its neutral form in Pt-Nafion. At the intersecting point in Fig. 1, the current obtained by a chronoamperometry measurement must be equal to the steady state current, though the former value can be estimated by extrapolation. Using Eqs. 2 and 3,

$$I_s = nFAlc_{At}/\pi t_l. \tag{8}$$

Substituting the values into I_s, n, F, A, l, and t_l in Eq. 8, c_{At} becomes 0.16 mol dm^{-3}, which is close to 0.15 mol dm^{-3}, the concentration in the contacting solution. From the above discussion it is concluded that the above assumption, that c_{At} is equal to the concentration of the contacting solution within the experimental error in the concentration range examined here, is acceptable and that there exists neither a specific affinity nor a repulsion between Nafion and ascorbic acid in the present system, though a strong affinity was often reported between organic substances and ion exchange membranes.

In the model of Fig. 2, the followings are applicable:

$$x + y = 0.0139, \tag{9}$$

$$J_{Fe} = 2\,J_{AA}, \tag{10}$$

$$\text{The flux of AA, } J_{AA} = D_{AA}c_{At}/x, \tag{11}$$

and

$$\text{The flux of } Fe^{3+},\ J_{Fe} = D_{Fe}c_{Fe}/y, \tag{12}$$

From the above equations,

$$y = D_{Fe}c_{Fe}\times0.0139/(2D_{AA}c_{At} + D_{Fe}c_{Fe}). \tag{13}$$

The calculated values of y are plotted as a function of c_{At} in Fig. 3. Using the values for y and Eq. 2, the oxidation current of AA was calculated and is described in Fig. 4 (open circle, solid line) together with the experimental results (triangle and black circle). The experimental values are smaller than the calculated values. The difference can partly be ascribed to the exclusion of Fe^{3+} by H^{+} formed by the oxidation of AA from the membrane.

In the above treatment, it was assumed that the reaction between AA and Fe^{3+} proceeded instantaneously at the surface where two species met. The concept of a reaction zone was introduced in order to examine whether the model of instantaneous reaction between Fe^{3+} and AA is valid or not. The model shown in Fig. 5 describes the reaction zone. The concentration of reactants is assumed to be uniform inside the zone (thickness; d) and equal to each other (c_{av}).

$$\mathrm{d}c/\mathrm{d}t = k_1 c_{\mathrm{av}}^2 \tag{14}$$

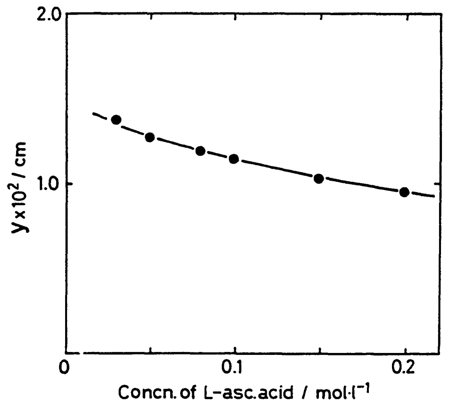

Fig. 3. The dependence of the thickness of diffusion layer for AA (y) on the concentration of AA in c.e.c. on Pt–Nafion 125 incorporated with Fe(3+/2+) redox couple (x+y=139 μm).

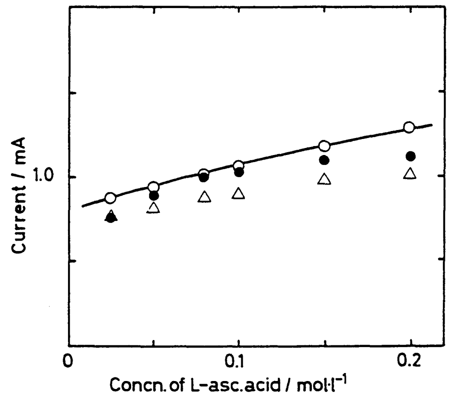

Fig. 4. Dependencies of oxidation current of AA on the concentration of AA in c.e.c. using Pt–Nafion 125 incorporated with Fe(3+/2+) redox couple. Solid line: values calculated using y in Fig. 3 and D_{Fe} and D_{AA}.
△: Run 1, ●:Run 2.

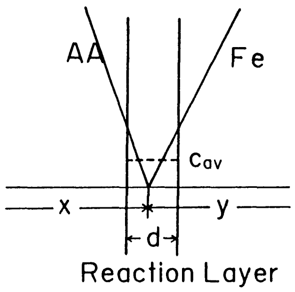

Fig. 5. A reaction layer model of indirect oxidation of AA on Pt–Nafion incorporated with Fe(3+/2+) redox couple.
d: reaction layer thickness, x: diffusion layer thickness of AA, y: diffusion layer thickness of Fe^{3+}, c_{av}: average concentration of AA and Fe^{3+}.

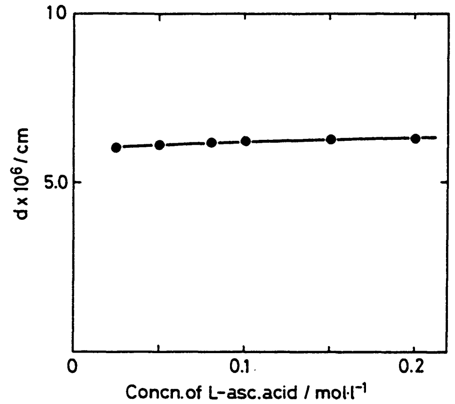

Fig. .6. The dependence of the reaction layer thickness (d in Fig. 5) on the concentration of AA in c.e.c. on Pt–Nafion 125 incorporated with Fe(3+/2+) redox couple.

Under a steady state,

$$k_1 c_{\mathrm{av}}^2 \times d/1000 = D_{\mathrm{AA}} c_{\mathrm{At}}/x. \tag{15}$$

A numerical calculation gave d, which is plotted in Fig. 6 as a function of c_{At}. As shown in the figure, the thickness is about 6 μm, about 4% of the Nafion thickness. This results reveals that the model of Fig. 2 is valid.

From the above discussion, it is shown that the rate of a mediated reaction is mainly controlled by the slow diffusion of AA and takes place within a narrow zone very close to the Nafion surface facing against c.e.c. Configuration a in Fig. 3 of Ref. 3, where substrates are contained in w.e.c., will make the diffusion pass of Fe^{3+} shorter and will remarkably enhance the reaction rate, though a direct reaction of substrates on the electrode bound on Nafion must proceed rapidly in this configuration.

Conclusion

Pt-Nafion incorporated with iron ions gave an example of a polymer coated electrodes containing redox mediators. Details of the concentration profiles of the reactants in the coating polymer, Nafion, were examined. A Fe^{2+}/Fe^{3+} redox couple incorporated into Pt-Nafion worked as a mediator in the oxidation of ascorbic acid. The diffusion of Fe^{3+} and AA was rate-determining, and the diffusion of the latter was slower. The mediation reaction proceeded in the very narrow zone, quite close to the Nafion surface. The averaged diffusion coefficients in Nafion, D_{Fe} and D_{AA}, were 1.5×10^{-7} cm^2 s^{-1} and 4.7×10^{-8} $cm^2 s^{-1}$, respectively. Ascorbic acid did not show any specific affinity to Nafion.

SPE composite electrodes were functionalized by the incorporation of mediator systems into SPE materials. This modification is expected to enhance its activity and reaction selectivities in its application to organic electrochemistry, sensors, etc. Configurations in which substrates are contained in the w.e.c. will enhance the activity of SPE composites electrodes incorporated with mediators.

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 61850147) from the Ministry of Education, Science and Culture.

References

1) Z. Ogumi, H. Yamashita, K. Nishio, Z. Takehara, and S. Yoshizawa, *Electrochim. Acta,* **28**, 1687 (1983).

2) Z. Ogumi, S. Ohashi, and Z. Takehara, *Nippon Kagaku Kaishi,* **1984**, 1788.

3) Z. Ogumi, T. Mizoe, N. Yoshida, and Z. Takehara, *Bull. Chem. Soc. Jpn.,* **60**, 4233 (1987).

4) I. Rubinstein and A. J. Bard, *J. Am. Chem. Soc.,* **102**, 6641 (1980).

5) D. A. Buttry and F. C. Anson, *J. Am. Chem. Soc.,* **104**, 4824 (1982).

6) E. W. Kristensen, W. G. Kuhn, and R. M. Wightman, *Anal. Chem.,* **59**, 1752 (1987).

7) C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.,* **142**, 1 (1982).

8) C. P. Andrieux and J. M. Saveant, *J. Electroanal. Chem.,* **93**, 163 (1978).

9) W. G. Grot, G. E. Munn, and D. N. Walmsley, 141st National Meeting, The Electrochemical Society, Houston, Texas (1972).

10) A. J. Bard and L. R. Foulkner, "Electrochemical Methods," John Wiley & Sons, New York (1980), Chap. 7.

11) H. L. Yeager and A. Steck, *J. Electrochem. Soc.,* **128**, 1880 (1981).

12) A. J. Bard and L. R. Foalkner, "Electrochemical Methods," John Wiley & Sons, New York (1980), Chap. 5.

13) M. M. T-Khan and A. E. Martell, *J. Am. Chem. Soc.,* **86**, 4176 (1967).

14) H. L. Yeager and B. Kipling, *J. Phys. Chem.,* **83**, 1836 (1979).

15) C. R. Martin and H. Freiser, *Anal. Chem.,* **53**, 904 (1981).