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Application of the SPE Method to Organic Electrochemistry-X. Behaviors of the Manganese Redox Couple Incorporated in Pt–Nafion and Their Mediatory Oxidation of Cinnamyl Alcohol to Cinnamaldehyde

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The electrochemical behavior of a manganese redox couple incorporated into an SPE (Solid Polymer Electrolyte) composite electrode using Nafion (Pt-Nafion) was examined as a mediator for electroorganic syntheses. The mediatory reaction of the redox couple was examined in the oxidation of cinnamyl alcohol. The oxidation proceeded smoothly and gave cinnamaldehyde in high selectivity; the current efficiency was as high as 85%. The dissolving-out of manganese from the SPE was suppressed by the addition of 0.025 mol dm^{-3} $MnSO_4$ to the catholyte.

The present authors have investigated the application of the SPE method to organic electrochemistry using Nafion as an SPE material.[1,2] The introduction of mediatory systems into an SPE electrolyzer is attractive because of an enhancement in both the selectivities and reaction rates. A high reaction selectivity would lower the contamination in SPE materials, leading to an extension of the life of SPE composite electrodes and to a low cell voltage. The applicability of mediatory systems to an SPE electrolyzer system was clarified in our previous studies using an iron redox system.[3,4] In the use of mediatory systems the mediator is apt to cause product contamination, which should be avoided. The situation is the same in the SPE system, where mediators are added into the substrate solution.[5,6] It is attractive to incorporate a mediator into an SPE composite electrode, since it might reduce the required amount of mediator and eliminate the product contamination.

In the present work a manganese redox couple was selected. Manganese dioxide is well known as a selective oxidizing reagent of allyl alcohol to the corresponding aldehyde, while keeping olefinic double bonds unchanged.[7–9] Among the different types of manganese dioxide, electrolytic manganese dioxide exhibits high activity. The electrolytic manganese dioxide is expected to be easily formed in situ from Mn^{2+} by anodic oxidation. Cinnamyl alcohol was selected as a substrate. The manganese redox system is expected to be prevented from dissolving out from the SPE material (Nafion) since Mn(IV), which is the oxidized half of the redox couple, must exist in the form of an oxide in the Nafion and multivalent cations including Mn^{2+}, which is the reduced half of the redox couple, have a higher ion-exchange affinity to the Nafion than does proton. This high affinity keeps the redox system inside the composite electrode.

Experimental

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

Pt-Nafion Composite Electrodes. Nafion 415 (product of du Pont Co.) was used as an SPE material. Platinum was deposited on one side of Nafion employing a previously described[10] electroless plating method. Mn^{2+} was introduced into Pt-Nafion from an aqueous manganese sulfate solution in the same manner as the cases of Fe^{2+} and Fe^{3+}.[3]

Electrolysis. A two-compartment cell divided by an SPE composite electrode was used for electrolysis. The cell was equipped with a Luggin capillary in the CEC, as described in a previous paper.[3] Conventional potentiostatic and galvanostatic electrolysis systems comprising a potentiostat (Hokuto Denko HA-301), a function generator (Hokuto Denko HB-104), and a recorder (Graphtec WX2400) were used.

Preceding the introduction of a substrate solution, Mn,Pt-Nafion was electrolyzed at 5 mA cm^{-2} in 0.025 mol dm^{-3} H_2SO_4 in CEC and argon in WEC for 15 coulomb in order to oxidize incorporated Mn^{2+} to MnO_2.

Since cinnamyl alcohol and cinnamaldehyde are hardly soluble in water, THF, which was stable under experimental conditions, was used as a solvent.

Results and Discussion

The principle regarding the mediatory electrochemical oxidation of alcohol in Pt-Nafion is schematized in Fig. 1 using cinnamyl alcohol as an example.

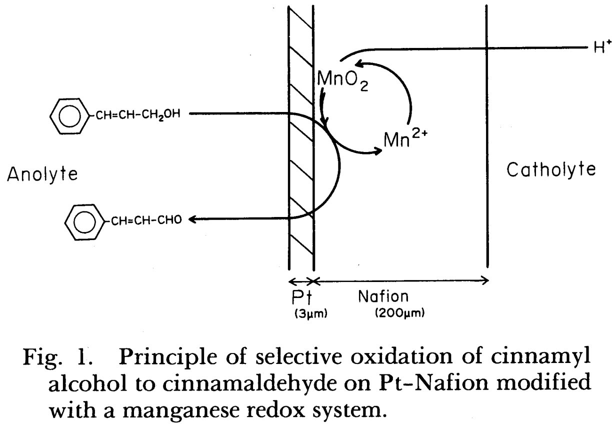

Fig. 1. Principle of selective oxidation of cinnamyl alcohol to cinnamaldehyde on Pt-Nafion modified with a manganese redox system.

Inside SPE, divalent manganese, Mn(II), is oxidized to tetravalent manganese, Mn(IV), on a thin porous anode bound to the SPE. Mn(IV) oxidizes the alcohol, which is penetrated through the porous anode layer from working electrode compartment (WEC, left). The alcohol is oxidized to the corresponding aldehyde, which returns to WEC. The proton released by the oxidation of the alcohol moves to the counter electrode compartment (CEC, right) across the Nafion layer under an electric field. This movement sustains the ionic conductivity through Mn,Pt-Nafion. The resultant Mn(II) is re-oxidized on the porous platinum anode. Thus, the manganese redox system mediates the oxidation of cinnamyl alcohol.

Incorporation of Manganese into Pt-Nafion. The exchange selectivity was examined using Nafion 125 and 117 in the same way as in a previous study.[3] Since they do not have any backing and have smooth surfaces, it was convenient to calculate their exchange capacity. As shown in Fig. 2, the exchange selectivity of Mn^{2+} to H^+ for Nafion 117 was higher than that for Nafion 125. Above 0.3 mol dm^{-3} of $MnSO_4$ concentration of a soaking solution, equivalent ionic fraction of Mn^{2+} as a counter ion of Nafion 117 was higher than 0.85. The Nafion 415 adopted here as an SPE material for electrolysis has the same equivalent weight as that of Nafion 117. Therefore, the Nafion 415 of composite electrodes exchanges its counter ion to Mn^{2+} to an extent higher than 0.85 by soaking in a solution containing Mn^{2+} at a concentration higher than 0.3 mol dm^{-3}.

Cyclic Voltammetry Measurements. Figure 3 shows a cyclic voltammogram obtained at Pt-Nafion incorporated with Mn^{2+} using 0.025 mol dm^{-3} H_2SO_4 in CEC, argon gas in WEC at the sweep rate of 10 mV s^{-1}. A couple of anodic (E_{ap}=1.22 V) and cathodic (E_{cp}=0.92 V) peaks were observed. Since no active species was added, except for a manganese species, and the circumstances inside Nafion are strongly acidic, these peaks should be ascribed to the oxidation of Mn^{2+} to MnO_2 and reduction of MnO_2 to Mn^{2+}.[11,12] These redox peaks were observed after repeated cycles. It is known that Mn^{3+} is produced in a strongly acidic solution. The potential of Mn^{3+} is as high as 1.51 V vs. NHE.[12] Therefore, the present redox peaks do not correspond to a reaction including Mn^{3+}. After anodic polarization, MnO_2 must be formed inside the Pt-Nafion. It was not successful, however, to observe peaks corresponding to MnO_2 in an X-ray diffraction analysis. This might be ascribed to the ambiguous crystallinity of the manganese oxide produced. Manganese oxide produced by an electrochemical method

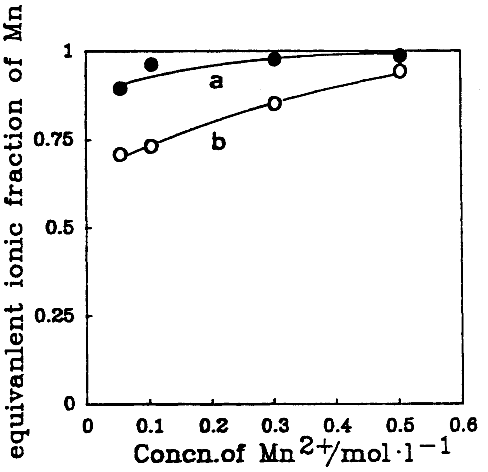

Fig. 2. The amount of manganese up-taken into Nafion 117 (a) and 125 (b) after soaking H-type membranes in a $MnSO_4$ solution in 0.025 mol dm^{-3} H_2SO_4.

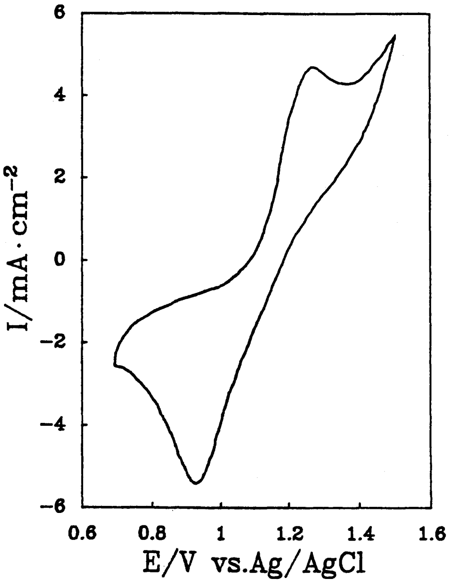

Fig. 3. Cyclic voltammograms (first cycle) on Mn,Pt-Nafion under argon in WEC and 0.025 mol dm^{-3} H_2SO_4 in CEC at 10 mV s^{-1}.

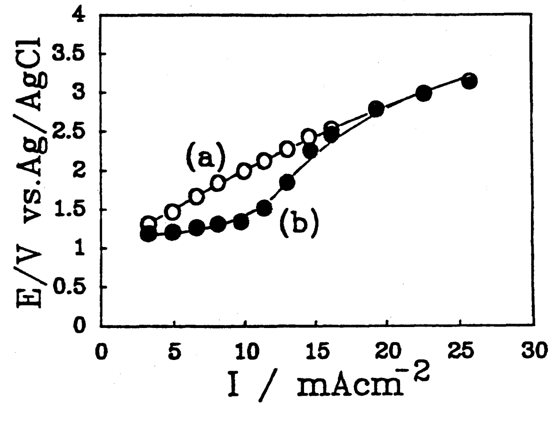

Fig. 4. Steady state polarization curves on Pt-Nafion (a) and Mn,Pt-Nafion (b) in cinnamyl alcohol 50% in THF in WEC and 0.025 mol dm^{-3} H_2SO_4 in CEC.

is known to give ambiguous X-ray diffraction patterns and to be active in the oxidation of organic substrates.

Steady-State Polarization. Steady-state polarization curves for Pt-Nafion both with and without the incorporation of Mn^{2+} were obtained in 50% cinnamyl alcohol in THF; the results are shown in Fig. 4. In the absence of manganese, the anode potential increased monotonously beyond 2.5 V with the current density. The values of the measured potential include the ohmic drop through the Nafion layer. This result indicates a large resistance of the Nafion, which may be caused by a contamination of the by-products from the substrate or solvent THF. It is also known that some organic solvents like methanol decrease remarkably the ionic conductivity of Nafion.[13] On the other hand, in the presence of a manganese mediatory system, the potential was, up to the current density of 15 mA cm^{-2}, kept lower than the value in the absence of the manganese redox. Beyond this current density, the potential increased rapidly up to the value without any incorporation of manganese (black circle). It was inferred from the electrode potential (lower than 1.3 V) that the oxidation of Mn^{2+} is a primary anodic reaction at a current density lower than 15 mA cm^{-2}. Beyond 17 mA cm^{-2}, two polarization curves were in coincidence with each other. This fact implies that the same reaction took place on the electrode at a current density higher than 17 mA cm^{-2}. At a high current density gas evolution was observed on both electrodes. Judging from the potential (higher than 2 V, with allowance for the uncompensated ohmic drop) these gas evolutions are ascribed to oxygen evolution. The transition to higher potential, between 12—17 mA cm^{-2}, is similar to the phenomenon observed in the Kolbe-type electrochemical reactions on a Pt electrode. The details of the inhibition proceeding at the lower current density in Fig. 4 have not been clarified yet.

Potentiostatic Oxidation of Cinnamyl Alcohol. The manganese oxide formed electrochemically inside Pt-Nafion was expected to be active in the oxidation of allyl alcohol to the corresponding aldehyde. The current efficiencies of cinnamaldehyde and cinnamic acid were measured using Pt-Nafion both with (Mn,Pt-Nafion) and without the incorporation of a manganese redox system and in THF. As shown in Fig. 5, the incorporation of a manganese redox system enhanced the current efficiency of cinnamaldehyde to a value as high as 85%, while lowering that of cinnamic acid. Thus, the selectivity for aldehyde was remarkably enhanced. In the potential region examined, no oxygen evolution was observed and, hence, Mn^{2+} was oxidized to MnO$_2$. Considering the results of polarization measurements shown in Fig. 4, an enhancement of current efficiency for aldehyde production by incorporating manganese should be ascribed to contribution from indirect oxidation by MnO$_2$. The mediation mechanism of the manganese redox system described in Fig. 1 has been shown to work well in the present Mn,Pt-Nafion.

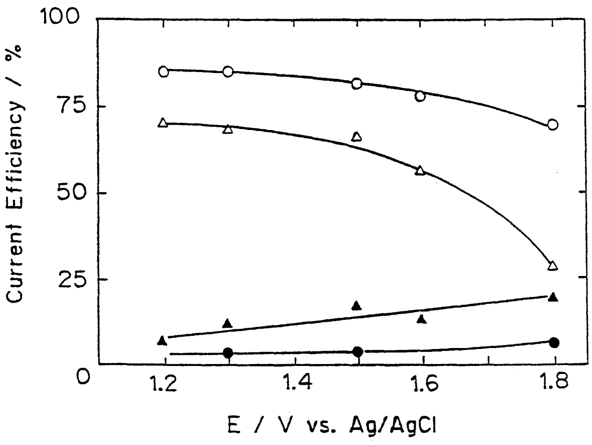

Fig. 5. Current efficiencies of cinnamaldehyde (open symbols) and cinnamic acid (black symbols) under potentiostatic electrolysis conditions in cinnamyl alcohol 50% in THF in WEC and 0.025 mol dm^{-3} H$_2$SO$_4$ in CEC on Mn,Pt-Nafion (circles) and Pt-Nafion (triangles).

Since the solubility of produced aldehyde into aqueous solution is very low,[14] and its mobility is much smaller than that of proton, the loss of aldehyde due to its permeation through the Nafion layer to CEC was retarded. After the reaction, no aldehyde was detected in CEC.

Dissolving out of Incorporated Manganese Redox Couple. The amount of incorporated mediator in SPE composite electrodes was limited to a very small amount due to the small thickness of the SPE material. The dissolving out of manganese species would cause a loss of the mediatory action and the contamination in produced aldehyde. The amounts of manganese dissolved out into WEC and CEC under potentiostatic electrolysis conditions at 1.4 V were examined by atomic absorption spectroscopy. The results are

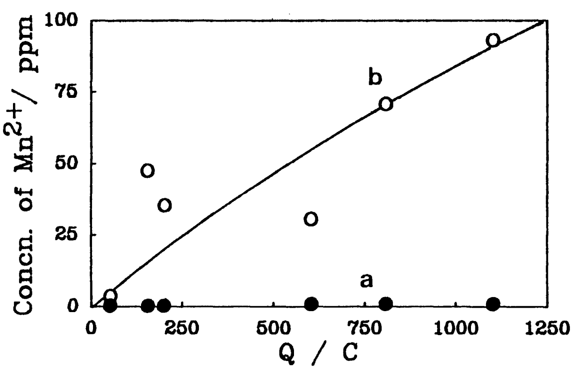

Fig. 6. Dissolving out of manganese from Mn,Pt-Nafion into CEC during potentiostatic electrolysis at 1.4 V in cinnamyl alcohol 50% in THF in WEC (14 cm^3) (a) and 0.025 mol dm^{-3} H$_2$SO$_4$ in CEC (14.5 cm^3) (b).

listed in Fig. 6. In the figure, 100 ppm means that about 10% of the incorporated manganese dissolved out. As shown in this figure, dissolving out into WEC was negligible, i.e., no contamination of the products by manganese occurred. On the other hand, the dissolving out of manganese into CEC increased with increasing charge passed, since the flux of ions in the Nafion was directed to the CEC under electrolysis conditions and since the ion-exchange affinity, as indicated in Fig. 2, was not sufficiently high for Mn^{2+} to be fixed inside the Nafion. This dissolving out would cause a loss of the mediator from an SPE composite electrode. It is acceptable to add Mn^{2+} in CEC, since it does not contaminate the product and Mn^{2+} is not reduced on the cathode. However, if the equilibrium concentration of Mn^{2+} in the Nafion became high, MnO_2 in the SPE composite electrode would accumulate during anodic polarization. Such accumulation might have an unfavorable influence and hinder the smooth indirect oxidation of alcohol. Therefore, the concentration of Mn^{2+} must be well optimized. The amount of manganese inside the Pt-Nafion was kept at the adequate level by the addition of manganese sulfate into CEC at a concentration of 0.025 mol dm^{-3}. At this concentration, the dissolving out of Mn^{2+} into CEC was well balanced with its returning into the Nafion due to its ion-exchange affinity; thus, the mediatory oxidation proceeded smoothly for more than 24 hours.

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