Application of the SPE Method to Organic Electrochemistry. XI. Influence of the Solvent on the Electrooxidation of Cinnamyl Alcohol on Mn,Pt-Nafion

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The influence of organic solvents on the electrooxidation of cinnamyl alcohol on Mn,Pt-Nafion has been investigated. Though tetrahydrofuran (THF) gave a high current efficiency (90%), carbon tetrachloride gave a low current efficiency (<20%). The importance of a co-solvent for the SPE electrolyzer was proposed and substrate transport to the active site located at the interface platinum/ionic cluster region was enhanced by solvents miscible with water. Though THF behaved as a good co-solvent, carbon tetrachloride did not. A composite electrode deposited with platinum on both surfaces of Nafion was applied to oxidation. The cell voltage was as low as 2 V.

The authors have reported that the application of mediatory systems into SPE (Solid Polymer Electrolyte) electrolyzers is both effective and attractive.[1-3] In a previous paper Mn,Pt-Nafion (a manganese redox system incorporated inside Pt-Nafion prepared by the deposition of a porous platinum electrode on Nafion) was applied to the selective oxidation of cinnamyl alcohol to cinnamaldehyde.[4] Both the current efficiency and selectivity to the aldehyde were remarkably enhanced by the addition of the manganese mediatory system.

The electrode reaction of this mediatory oxidation system is as follows:

$$Mn^{2+}+2H_2O \longrightarrow MnO_2+4H^+ +2e^-. \qquad (1)$$

The MnO_2 formed in this reaction reacts with the alcohol while giving aldehyde and regenerating Mn^{2+}.[5] As shown by the oxidation potential of MnO_2 described in the following equation, the activity of MnO_2 is strongly dependent on such solution properties as the pH and water content:

$$E=E^0+\frac{RT}{2F}\ln\frac{a_{MnO_2}(a_{H^+})^4}{a_{Mn^{2+}}(a_{H_2O})^2}. \qquad (2)$$

In the present work, the effect of the solvent was examined in detail.

Regarding SPE electrolyzers, it is expected that the cell voltage can be decreased by decreasing the gap between the anode and cathode. Composite electrodes deposited with an electrode on both surfaces of SPE materials would limit the electrode gap to the thickness of the SPE material. This type of composite electrode was also examined in the selective oxidation of cinnamyl alcohol.

Experimental

SPE Composite Electrodes. Pt-Nafion was prepared by the deposition of a porous platinum layer onto one surface of Nafion 415 utilizing an electroless plating method that employs hydrazine as a reductant. Details concerning the deposition method have been reported elsewhere.[6,7] Pt-Nafion-Pt, which is a composite electrode deposited with platinum on both surfaces of Nafion 415, was prepared by depositing a porous platinum layer on the second surface in the same manner as depositing one on the first surface. Incorporating a manganese redox system into Pt-Nafion and Pt-Nafion-Pt was achieved as described previously.[3,4]

Electrolysis. The experimental cell was described in a previous paper.[4] Electrolysis was carried out under potentiostatic or galvanostatic conditions.

In all experiments, 0.025 M (M=mol dm^{-3}) aqueous sulfuric acid containing 0.025 M manganese sulfate was used as a catholyte in a counter electrode compartment (CEC). Different kinds of anolytes were prepared and filled in a working electrode compartment (WEC).

Product mixtures were analyzed by an HPLC device (Hitachi 638-30) equipped with a Synchropak SCD column using internal standards.

The amount of manganese dissolved out was measured by atomic absorption spectroscopy after electrolysis under potentiostatic conditions at 1.4 V vs. Ag/AgCl.

Chemicals. All of the chemicals used were of reagent grade, and were used without further purification.

Results

Stability of Solvents. Four solvents (tetrahydrofuran (THF), diethyl ether, benzene, and carbon tetrachloride) were examined. These four solvents were stable on the anode under the experimental conditions. Since no product was isolate by HPLC, except for cinnamaldehyde and cinnamic acid, the main side reaction was considered to involve oxygen evolution.

Current Efficiency in Different Solvents. Using the four solvents, electrolysis was carried out at 1 mA cm^{-2} in 50 vol% cinnamyl alcohol, and 25 °C on Mn,Pt-Nafion. As described in Table 1, carbon tetrachloride gave the lowest current efficiency. Diethyl ether gave a current efficiency that was a little lower than THF. Benzene gave a medium value.

Since carbon tetrachloride showed the most pronounced decrease in the current efficiency, this solvent was examined in detail and compared with THF.

Table 1. Effects of Solubilities of Organic Solvents on the Current Efficiencies of Cinnamaldehyde, at 25 °C

	Solubility in water[a]	Current efficiencies/%
CCl_4	0.077	13
Benzene	0.178	63
Diethyl ether	6.04	72
THF	Inf.	85

a) g/100 g H_2O.

Steady State Polarization Curves. Figure 1 shows steady state polarization curves for 50 vol% cinnamyl alcohol in carbon tetrachloride and THF. Curve b, obtained in the presence of a manganese mediatory system in carbon tetrachloride, shows a lower potential at a low current density than does curve a, obtained in the absence of a mediatory system in carbon tetrachloride. The difference was much smaller than in the case of using THF as a solvent (curve c). This result suggests that the mediatory system did not work as effectively in carbon tetrachloride as in THF. This ineffectiveness lowered the current efficiency of aldehyde formation. Oxygen evolution was observed in carbon tetrachloride at a high current density.

The Influence of Substrate Concentration. Generally speaking, it is favorable to increase the substrate concentration for a higher performance of electrolyzers. The influence of the substrate concentration was examined using THF and carbon tetrachloride as solvents under potentiostatic electrolysis conditions at 1.5 V. The results are shown in Fig. 2. Using THF, the current efficiency of cinnamaldehyde remained almost unchanged up to an alcohol concentration of 50%, but decreased remarkably beyond 50%. Using carbon tetrachloride as solvent, the current efficiency of aldehyde formation was much lower than the value obtained for THF, and was dependent in a different way on the concentration; the current efficiency showed a maximum at ca. 70%. The production of cinnamic acid remained almost unchanged in both solvents and oxygen evolution was observed as a side reaction.

The influence of the solvent and substrate concentration on the mediatory action and oxidation efficiency was examined in more detail using a mixed solvent of THF and carbon tetrachloride. By fixing the substrate concentration at 50%, the ratio THF/carbon tetrachloride could be changed. As shown in Fig. 3, the current efficiency of the aldehyde increased upon increasing the THF/carbon tetrachloride ratio.

Influence of Current Density. If mass transport plays an important role in the electrochemical system, the current density would provide a major influence on the current efficiency. As shown in Fig. 4, the current efficiency of cinnamaldehyde decreased rapidly from 10 mA cm^{-2} using Mn,Pt-Nafion. On the other hand, the current efficiency of cinnamic acid remained unchanged upon increasing the current density.

The Stability of Mn,Pt-Nafion. The dissolving out of incorporated manganese was also measured using carbon tetrachloride as a solvent. This dissolving out was more remarkable, by 20 to 40%, in carbon tetrachloride than in THF.[4)]

Electrolysis Using Mn,Pt-Nafion-Pt. It is favorable to use an aqueous solution in CEC, since Nafion

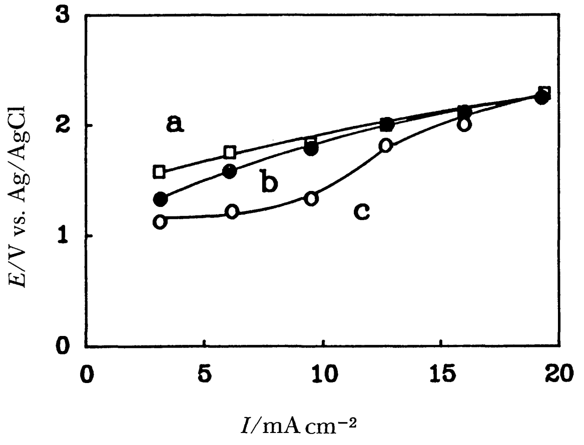

Fig. 1. Steady state polarization curves on Pt-Nafion (a), on Mn,Pt-Nafion (b) in 50 vol% cinnamyl alcohol in carbon tetrachloride, and on Mn,Pt-Nafion (c) in 50 vol% cinnamyl alcohol in THF.

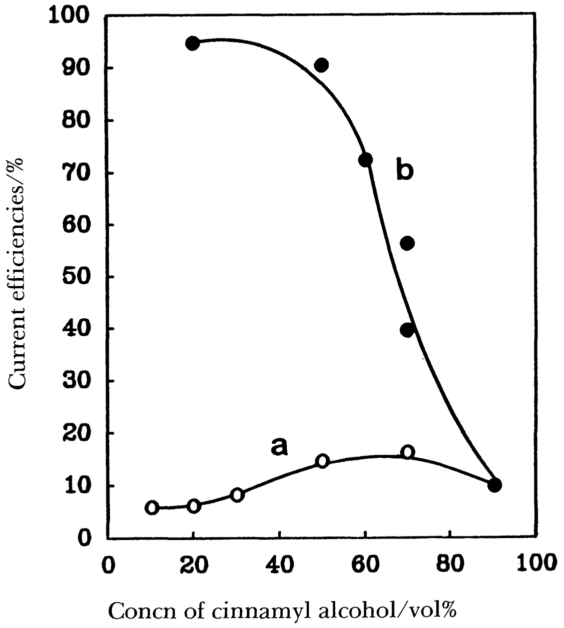

Fig. 2. Current efficiency dependencies of cinnamaldehyde production on cinnamyl alcohol concentration under potentiostatic electrolysis conditions at 1.5 V on Mn,Pt-Nafion.
a: carbon tetrachloride, b: THF.

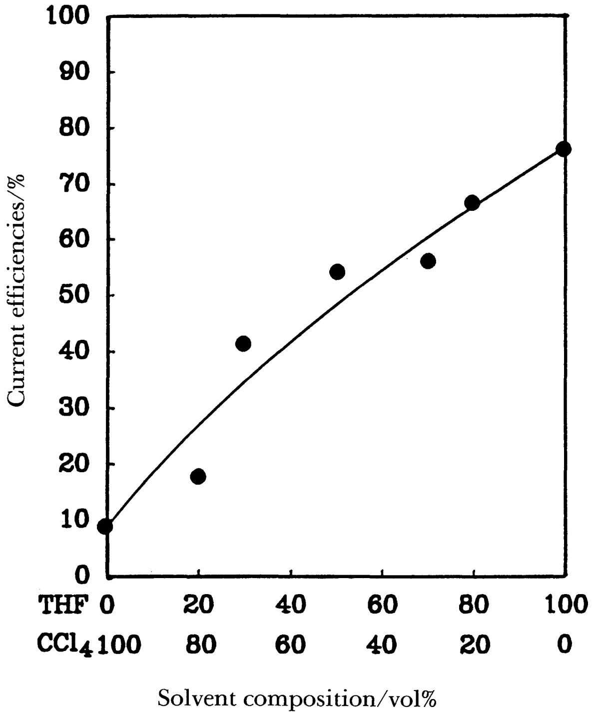

Fig. 3. The influence of THF/carbon tetrachloride ratio on the current efficiency of cinnamaldehyde under galvanostatic electrolysis conditions at 6 mA cm^{-2} on Mn,Pt-Nafion and 50 vol% cinnamyl alcohol in WEC.

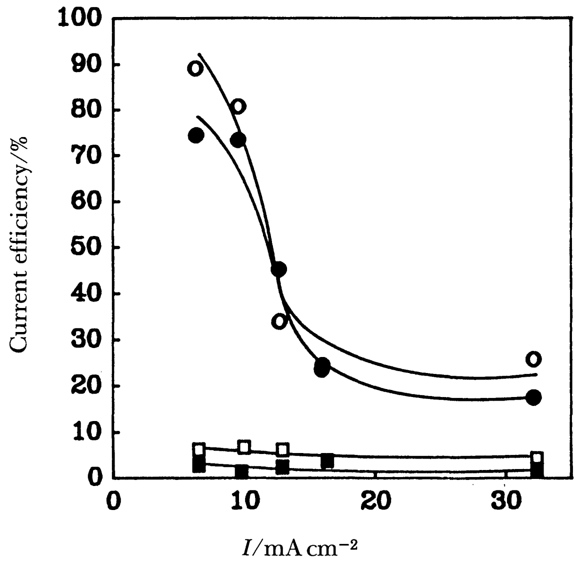

Fig. 4. Dependencies of current efficiency on current density.
open symbols: Mn,Pt-Nafion,
black symbols: Mn,Pt-Nafion-Pt,
circles: cinnamaldehyde, squares: cinnamic acid.

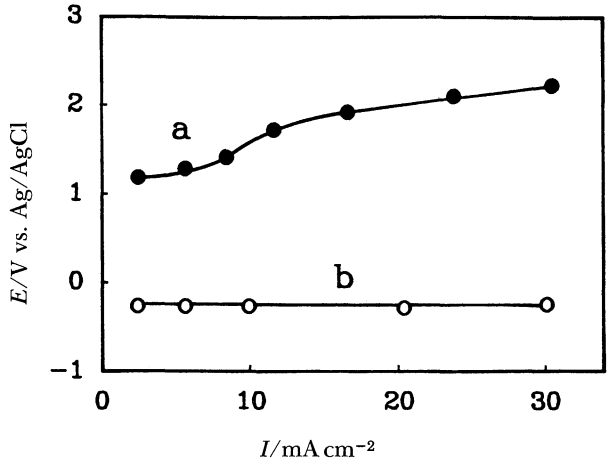

Fig. 5. Steady state polarization curves on Mn,Pt-Nafion-Pt in 50 vol% cinnamyl alcohol in THF.
(a): anode, (b): cathode.

is known to show ionic conductivity of a few orders of magnitude lower in organic solvents than in aqueous solutions.[8] Nafion shows a fairly high ionic conductivity under a humidified gas atmosphere, as investigated in fuel-cell applications. As described above and in a previous paper, the incorporated redox system tended to dissolve out into an aqueous solution in CEC. If no solution was used in the CEC, no dissolving out could occur. By using Mn,Pt-Nafion-Pt, a 50% cinnamyl alcohol solution in THF was electrolyzed. Argon was filled in CEC. The cell voltage was, however, very high for this electrolyzer and the cell temperature increased. This result suggests that the ionic conductivity of Nafion is very low under the electrolysis conditions. This type of electrolysis was not acceptable from practical viewpoints. An aqueous solution of 0.025 M sulfuric acid containing 0.025 M manganese sulfate was filled in the CEC in order to enhance the ionic conductivity of Mn,Pt-Nafion-Pt. Polarization curves for the anode and cathode are listed in Fig. 5. The electrode potential was measured using a Luggin capillary inserted in the CEC; the ohmic drop was not corrected. The difference in the anodic and cathodic potentials gives the cell voltage at each current density. At low current densities, where mediatory oxidation was predominant, the cell voltage was less than 2 V. The current efficiency for Mn,Pt-Nafion-Pt was compared with the results for Mn,Pt-Nafion. As shown in Fig. 4, Mn,Pt-Nafion-Pt showed a current efficiency change with an increase in the current density similar to that of Mn,Pt-Nafion. The current efficiency decreased abruptly at about 10 mA cm^{-2}. The critical current density corresponded to the value in the polarization curve in Fig. 5, beyond which oxygen evolution became significant.

Discussion

Electrochemical charge transfer reactions take place at the interface between electronic and ionic conductors. This was also true in the present electrochemical system. The structure of Nafion is accepted to be microscopically separated into two phases: a hydrophilic ionic cluster and a lipophilic polytetrafluoroethylene-like backbone.[9] H. L. Yeager and co-workers have pointed out that a majority of sorbed water is incorporated in an ionic cluster region of Nafion. The ionic cluster region in the membrane is regarded as being surrounded by a lipophilic environment.[10,11] These clusters are connected to each other by a small channel. Ionic conduction of SPE composite electrodes using Nafion is based on ionic migration through the ionic cluster region where most of the ionic groups (fixed ions and counter ions) and water taken up inside the Nafion exist. Since the deposition of a porous platinum electrode on Nafion was carried out in an aqueous solution, platinum likely at least contacted the ionic cluster region. The active site for charge transfer on an SPE composite electrode is located at the platinum/Nafion interface (the interface between the platinum and the hydrophilic ionic cluster region of Nafion), since the hydrophobic region of Nafion solves neither ionic charge carriers nor polar solvents.[12] In the present system, Mn^{2+} is oxidized there to form MnO_2, which must stay in the ionic cluster region (see Fig. 6). The substrate must be transported to the ionic cluster region in order to contact and react with MnO_2, where it is oxidized. As mentioned above, the ionic cluster region is strongly hydrophilic and is considered to be in the condition of an aqueous solution. Since cinnamyl alcohol is hardly soluble in water, it is difficult for the alcohol to enter this region. Some organic solvent is required in the ionic cluster region in order to help the alcohol to penetrate into the active region, the ionic cluster. Nafion swells not only solvents having a high solubility parameter, but also those having a low solubility parameter. It was proposed that solvents with a low solubility parameter interact with the hydrophobic site of Nafion.[13] The four solvents examined here have fairly low solubility parameters. The authors have proposed the existence of a path in the amorphous hydrophobic region of Nafion for the transport of oxygen.[14] This region is responsible for the interaction with hydrophobic solvents. Since cinnamyl alcohol is hardly soluble in water, it is acceptable to consider that the alcohol does not penetrate into the hydrophilic aqueous region but, rather, stays in the hydrophobic region. This hydrophobic region corresponds to the path for oxygen and allows hydrophobic substances to remain.[6,11,14] As mentioned above, cinnamyl alcohol must be transported from a hydrophobic site to the active site of the SPE composite electrode in order to react electrochemically (Fig. 6). The difference in the current efficiency of the four solvents examined can be explained in terms of their miscibility with water. When solvents for cinnamyl alcohol is immiscible with water, transport is very difficult and is not easily oxidized on Mn,Pt-

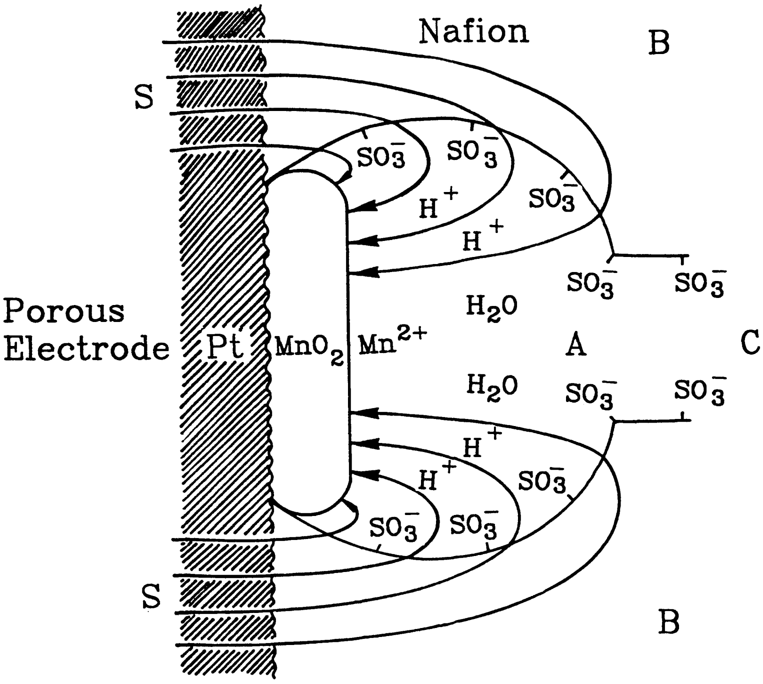

Fig. 6. Simplified schematic model of mass transfer to the active site on Mn,Pt-Nafion.
A: ionic cluster region, B: hydrophobic backbone region, C: channel, S: substrate.

Nafion. The solubilities of four solvents to water are listed in the same table. When THF is used as a solvent of anolyte, the aqueous catholyte and the anolyte mix with each other since Nafion is not a good separator for small neutral species8) and THF is freely soluble in water; THF behaves as a co-solvent of cinnamyl alcohol and water. This mixing would increase the solubility of the substrate alcohol so that alcohol can be transported into the ionic cluster, reach MnO_2, and be oxidized to aldehyde. The product, cinnamaldehyde, is insoluble in water and mixing also increases its mass transport. Such mixing, however, also enhances the mass transport of both the substrate alcohol and the product aldehyde to the catholyte, while their transport rates are expected to remain small. This transport would make the separation processes difficult, decreasing the merit of SPE electrolyzers.

Since carbon tetrachloride is insoluble in water, on the other hand, it can neither enter into an ionic cluster nor enhance the transport of the substrate alcohol to an ionic cluster, thus differing from the case of a THF solution. The current efficiency of aldehyde formation was therefore very low in the case of carbon tetrachloride.

Benzene, the solubility of which is lower in water than THF and diethyl ether and higher than carbon tetrachloride, gave a medium current efficiency. The results given in Table 1 suggest that a mixture of benzene with water produces a sufficient flux to support mass transport at a current density as low as 1 $mA\,cm^{-1}$. When the current density is increased using benzene as a solvent, the rapid decrease in the current efficiency observed in Fig. 4 using THF appeared at a current density of about half the value for THF; a mass-transfer limitation appeared at a much lower current density for benzene than for THF. Benzene can not support such a large mass-transfer flux to the active site in the same way that THF can. This fact supports the importance of the miscibility of the solvent for mass transport. Diethyl ether has a fairly high solubility in water and gives an efficiency slightly lower than that of THF.

The increase in the substrate concentration seems to enhance its flux to the active site. This was not the case in the present system. An increase in the substrate concentration leads to a decrease in the THF (co-solvent) content. Since the substrate transport is controlled by the concentration of co-solvent around the active site of the deposited platinum electrode, a decrease in the THF content leads to a retardation of the transport of cinnamyl alcohol to the active site, and therefore lowers the current efficiency (Fig. 2). The same consideration is applicable to the result given in Fig. 3, which was obtained by changing the THF/carbon tetrachloride ratio. The decrease in the ratio lowered the THF content in the ionic cluster. This fact made the transport more difficult, decreasing the current efficiency with a decrease in the ratio.

From the above discussion, the path through which the substrate is transported to the active site of SPE composite electrodes seems to have a very large influence on the efficiency. The path includes not only the ionic cluster region, but also the porous electrode layer deposited on the Nafion. The morphology of the deposited platinum, such as its shape, size, porosity, and thickness, as well as the penetration depth of the deposited platinum particles into the Nafion, must have a very large influence on substrate transport. In order to obtain reproducible SPE composite electrodes, platinum must be deposited under controlled conditions regarding pretreatment, reductant composition, chloroplatinic acid concentration, pH, and temperature.7) For example, the current density at which the reaction shifts from the mediatory oxidation of alcohol to oxygen evolution in a THF solution was dependent on the preparation process of the composite electrodes. On one electrode it was 12—13 $mA\,cm^{-2}$, and on the other it was 2—3 $mA\,cm^{-2}$. On the other hand, the potential at which the shift took place was independent of both the preparation process and the electrode morphology.

Conclusion

The influence of solvents on the electrooxidation of cinnamyl alcohol on Mn,Pt-Nafion was discussed. It is one of the merits of SPE electrolyzers that many different kinds of solvents can be used to dissolve the substrate. However, when an aqueous solution is used as a solution in CEC (that is favorable for electrolysis at a low cell voltage), a limitation in the selection of solvent arises in order to obtain a sufficient flux of substrate transport to the active site of the SPE composite electrode; a co-solvent for substrates and water is required. Solvents which are highly soluble in water, such as THF and diethyl ether, are useful. A composite electrode deposited with platinum on both surfaces of Nafion was applicable for the oxidation of cinnamyl alcohol. The cell voltage was as low as 2 V.

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