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Application of the SPE Method to Organic Electrochemistry. XII. Lead Dioxide as a Mediator for Electrooxidation of Cinnamyl Alcohol on Pt-Nafion

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Lead dioxide was examined as a mediator to oxidize cinnamyl alcohol on Pt-Nafion, and was compared with manganese dioxide. Lead dioxide was deposited into Pt-Nafion. The current efficiency for the formation of cinnamaldehyde reached 65% at room temperature, slightly lower than that in the case of using manganese dioxide. The production of cinnamic acid was more remarkable on Pb,Pt-Nafion than on Mn,Pt-Nafion because of the higher oxidation potential of the former. The mediatory action of both oxides was examined and compared with the activity in chemical oxidation using oxides produced separately. The oxidation of cinnamyl alcohol by lead dioxide was faster than that by manganese dioxide. Their mediatory action reflected their chemical activity for the oxidation.

Due to an inherently high oxidation potential[1,2] of the hydroxyl group, a variety of indirect procedures utilizing appropriate organic and inorganic chemicals as mediators have been devised for oxidizing the group.[3–6] We have reported in previous papers[7,8] that in a system comprising solid polymer electrolyte (SPE) electrolyzers, with Nafion as an SPE material, manganese dioxide deposited into Pt-Nafion behaves as a mediator and enhances the reaction selectivity of alcohol to the corresponding aldehyde.

As known, PbO_2 is widely used in practical rechargeable lead-acid batteries due to its high electrochemical reversibility and high oxidation potential under acidic conditions. These properties are attractive for use as an oxidizing reagent of organic substances. In the present study lead dioxide was focused as a mediator for indirect oxidation of cinnamyl alcohol using an SPE composite electrode prepared by depositing a porous platinum layer on Nafion, Pt-Nafion.[9] It was reported in our previous papers that Mn, Pt-Nafion prepared by incorporating manganese dioxide into Pt-Nafion as a mediator behaved as a good electrode for the selective oxidation of cinnamyl alcohol to cinnamaldehyde, while leaving C=C unchanged.[7] The activity and reaction selectivity of Pb,Pt-Nafion were compared with Mn,Pt-Nafion.

Since the oxidation of cinnamyl alcohol by a metal-oxide mediatory system involves an irreversible catalytic reaction following a reversible charge-transfer reaction producing reactive oxides on the anode, the chemical reactions between oxides (PbO_2 and MnO_2) and cinnamyl alcohol were also investigated in order to improve our understanding of the reaction systems.

Experimental

Electrochemical Oxidation. Pt-Nafion composite electrodes were prepared by an electroless deposition of a porous platinum layer on Nafion 417.[9] After platinum deposition, the Pt-Nafion was immersed in 1 mol dm^{-3} H_2SO_4 for more than 2 h in order to exchange the counter ion for H^+. This H^+-type Pt-Nafion was then immersed in a 0.5 mol dm^{-3} $Pb(NO_3)_2$ aqueous solution for more than 8 h in order to incorporate Pb^{2+} into Pt-Nafion. An electrolytic cell equipped with Pb,Pt-Nafion was described previously.[7] The effective geometric surface area of the anode was found to be 3.14 cm^2. The volumes of the working electrode (anodic) and the counter electrode (cathodic) compartments (WEC and CEC) were 6.5 cm^3 and 16 cm^3, respectively. The electrode potential was set vs. the Ag/AgCl reference electrode via a Luggin capillary inserted in a CEC using a potentio/galvanostat (Hokuto Denko HA-301). In all cases, the set potential was not corrected for both the junction potential at the interface between Nafion and the contacting solution and a fairly large ohmic drop through the Nafion.

Tetrahydrofuran (THF) was selected as a solvent. The concentration of cinnamyl alcohol was fixed at 50 vol% in THF. In order to suppress any dissolving out of Pb^{2+} into a CEC from Pt-Nafion, 0.05 mol dm^{-3} $Pb(NO_3)_2$ was added to a CEC containing 0.05 mol dm^{-3} HNO_3 during electrolysis.

Electrolysis was carried out using a conventional potentio/galvanostatic electrolysis set-up at 25 °C, except for those cases specified. The experimental details were identical to those described in a previous paper.[10]

Chemical Reactions. Electrolytic manganese dioxide (EMD) was donated by Mitsui Mining and Smelting Co., Ltd. Because of the low chemical activity of commercially available lead dioxide, freshly prepared lead dioxide was utilized for chemical reactions.[11] The fresh, active lead dioxide was prepared by decomposition of lead tetraacetate.[12] Then, 50 g of lead tetraacetate was added to 500 cm^3 of water under stirring. It decomposed to brown lead dioxide precipitates. The crude lead dioxide was washed with 100 cm^3 of water 4 times and filtered under suction, followed by washing with 50 cm^3 of acetone 4 times. The yield of a dark-brown powder of lead dioxide was about 20 g. Cinnamyl alcohol (0.2 g) was stirred with a suspension of excess amount of EMD (0.5 g) or PbO_2 (2 g) in acetone (50 cm^3) or in acetone (50 cm^3) containing 0.4 mol dm^{-3} sulfuric acid and 4% water at a fixed temperature.

Analysis. The products were analyzed by an HPLC device (Hitachi 638-30) equipped with a Synchropak SCD 100 column. 4-Nitrotoluene was selected as an internal standard.

Results and Discussion

Electrochemical Behaviors of Pb,Pt-Nafion. In order to examine the electrochemical behaviors of a lead redox couple in Pt-Nafion, cyclic voltammetry measurements were conducted. The cyclic voltammogram on Pb,Pt-Nafion in 0.05 mol dm^{-3} HNO_3 in a CEC (curve a of Fig. 1) was compared with that on Mn,Pt-Nafion in 0.025 mol dm^{-3} H_2SO_4 in a CEC (curve b of Fig. 1). Ar gas was filled in a WEC in both cases. An anodic plateau (E_{ap}=1.42 V) and a cathodic peak (E_{cp}=1.22 V) appear on curve a. The peak separation was fairly large (200 mV) because of an uncorrected ohmic drop caused by the low conductivity of Nafion. This peak and plateau correspond to a reduction and oxidation of the lead redox couple. Oxygen evolution began at a potential close to lead dioxide formation (E>1.50V), according to curve a. Although the deposition of lead dioxide on Pt-Nafion enhanced the oxygen overvoltage, this enhancement was not as large as was expected. On the other hand, Mn,Pt-Nafion gave a better-defined cyclic voltammogram, although the peak separation was still large. Pb,Pt-Nafion gave higher redox peaks, by about 200 mV, than Mn,Pt-Nafion, as was expected from their standard redox potentials reported (1.45 V and 1.23 V vs. NHE, respectively).

Figure 2 shows anodic polarization curves under quasi-steady state conditions for Pb,Pt-Nafion (curve a,c), which were compared with those for Mn,Pt-Nafion (curve b,d). The electrode potentials for Pb,Pt-Nafion were higher than those for Mn,Pt-Nafion in two systems: with (curve a,b) and without (curve c,d) cinnamyl alcohol in a WEC. Even in the presence of alcohol, the potentials of both electrodes were kept low at current densities lower than 2 mA cm^{-2}. This was ascribed to the proceeding of mediatory oxidation processes on both electrodes: the primary electrode reaction involved the oxidation of two metal ions regenerated by reactions of the metal oxides with the alcohol in a low-current density region.

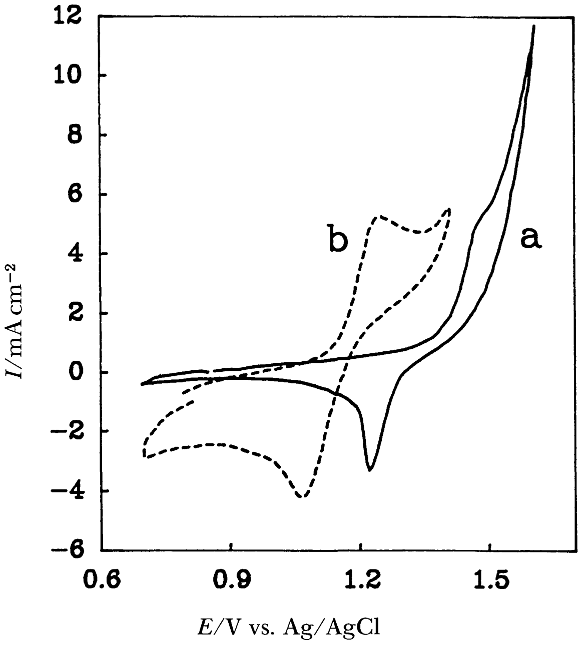

Fig. 1. Cyclic voltammograms (a); on Pb,Pt-Nafion, 0.05 mol dm^{-3} HNO_3 in CEC, (b); on Mn,Pt-Nafion, 0.025 mol dm^{-3} H_2SO_4 in CEC, W.E.C: Ar, at 10 mV s^{-1}.

$$Pb^{2+} + 2H_2O = PbO_2 + 4H^+ + 2e^- \quad 1.45\ \text{V vs. NHE} \qquad (1)$$

$$Mn^{2+} + 2H_2O = MnO_2 + 4H^+ + 2e^- \quad 1.23\ \text{V vs. NHE} \qquad (2)$$

$$C_6H_5CH{=}CHCH_2OH + MO_2 + 2H^+ =$$
$$\text{(acidic)} \quad C_6H_5CH{=}CHCHO + M^2 + 2H_2O \qquad (3)$$

$$C_6H_5CH{=}CHCH_2OH + MO_2 =$$
$$\text{(neutral or basic)} \quad C_6H_5CH{=}CHCHO + M(OH)_2 \qquad (4)$$

(M=Pb or Mn)

On the other hand, when electrolytic current density exceeded 2 mA cm^{-2}, the anodic potential gradually shifted to the positive direction and reached the value for oxygen evolution on both electrodes. Gas evolution was observed on both electrodes at high current densities. The potential for oxygen evolution was higher on both electrodes in the presence of alcohol (a,b) than in its absence (c,d). This might be caused by a poisoning of the electrodes by by-products from the substrate or solvents which were not detected, though, in HPLC analysis. The by-products might decrease the ionic conductivity of Nafion and enhance the uncorrected ohmic drop. This poisoning was also suggested by a potential change during electrolysis. As shown in Fig. 3, the anode potential of Pb,Pt-Nafion gradually increased, even at a current density

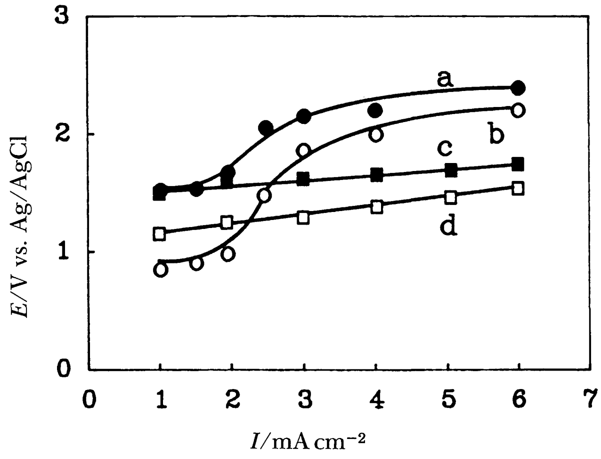

Fig. 2. Steady state polarization curves on Pb,Pt-Nafion (a, c) and Mn,Pt-Nafion (b, d).
Solutions in CEC were the same as in Fig. 1.
a, b: cinnamyl alcohol 50% in THF in WEC. c, d: Ar in WEC.

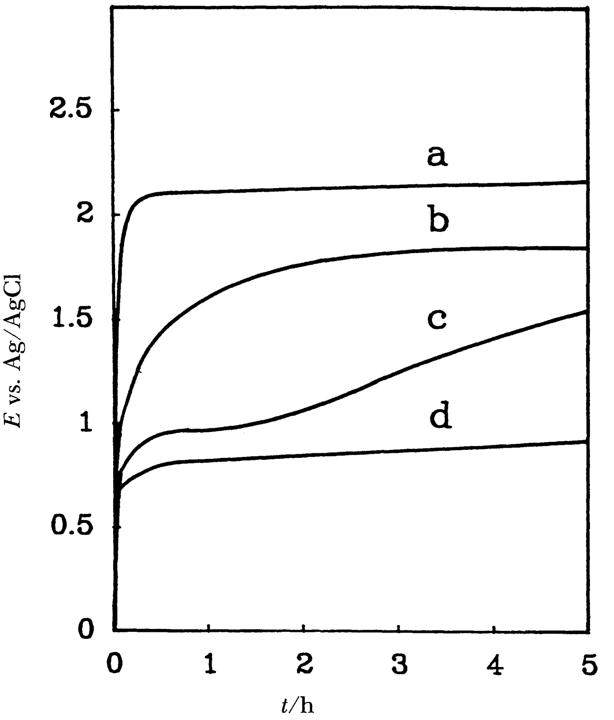

Fig. 3. Potential changes during electrolysis on Pb,Pt-Nafion under galvanostatic electrolysis conditions in cinnamyl alcohol 50% in THF in WEC at 25 °C.
a: 4, b: 3, c: 2, d: 1 mA cm^{-2}.

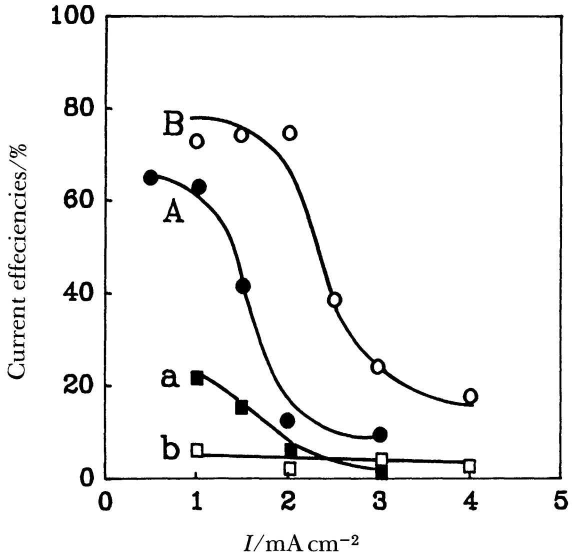

Fig. 4. Current efficiencies of cinnamaldehyde (A, B) and cinnamic acid (a, b) under galvanostatic electrolysis conditions in cinnamyl alcohol 50% in THF in WEC on Mn,Pt-Nafion (B, b) and Pb,Pt-Nafion (A, a).

as low as 2 mA cm^{-2}, and reached the potential necessary for oxygen evolution, although its change was very slow at a very low current density of 1 mA cm^{-2}. A similar potential change was also observed for Mn,Pt-Nafion. In addition to the above-mentioned reasons, it was reported that the ionic conductivity of Nafion was remarkably decreased in some organic solvents.[13)]

Galvanostatic Oxidation of Cinnamyl Alcohol. As reported in a previous paper,[7)] the reaction selectivity for aldehyde formation was remarkably enhanced by the incorporation of a manganese redox couple into Pt-Nafion.The current efficiency of the oxidation of cinnamyl alcohol using Pb,Pt-Nafion was examined under galvanostatic electrolysis conditions. The results are given in Fig. 4 (curves A and a), together with the results using Mn,Pt-Nafion (curves B and b). At low current densities, cinnamaldehyde was produced in high current efficiency (A), which, however, slightly lower than that on Mn,Pt-Nafion (B). On the other hand, the efficiency of cinnamic acid production on Pb,Pt-Nafion (a) was higher at low current densities than that on Mn,Pt-Nafion (b). On both composite electrodes the current efficiency for aldehyde formation decreased upon increasing the current density, although the decrease began at a lower current density on Pb,Pt-Nafion (A) than that on Mn,Pt-Nafion (B). On the former electrode acid production reached 20% at a low current density and then decreased with an increase in the current density; however, it was low, and almost unchanged, on the latter electrode. The rapid decrease in the current efficiencies on the former should be ascribed to easier oxygen evolution since the potential of oxygen evolution was closer to that of lead dioxide formation than on the latter electrode (Fig. 1). The higher efficiency of acid formation on Pb,Pt-Nafion than that on Mn,Pt-Nafion should be ascribed to the more positive potential of lead dioxide (ca. 200 mV) than that of manganese dioxide.

Since no organic by-product was detected on HPLC and gas chromatography analyses, only oxygen evolution was considered to exist as a side reaction.

Oxidation was also affected by the electrolysis temperature. As shown in Fig. 5, the current efficiencies of aldehyde formation increased upon increasing the temperature on both Mn,Pt-Nafion and Pb,Pt-Nafion at 1.5 mA cm^{-2}. At high temperature the reaction between mediator oxides and the alcohol became faster and the mediatory reaction proceeded more smoothly. Thus, the current efficiency of aldehyde formation increased on both electrodes upon increasing the temperature. The current efficiency of cinnamic acid formation increased on Pb,Pt-Nafion with a temperature increase, whereas on Mn,Pt-Nafion it remained almost unchanged with a temperature change, while maintaining a low value. This result suggests that a high potential is necessary for the oxidation of the alcohol to the corresponding acid, and that the potential of MnO_2 was not sufficiently high to oxidize the alcohol to acid. N.L. Weinberg

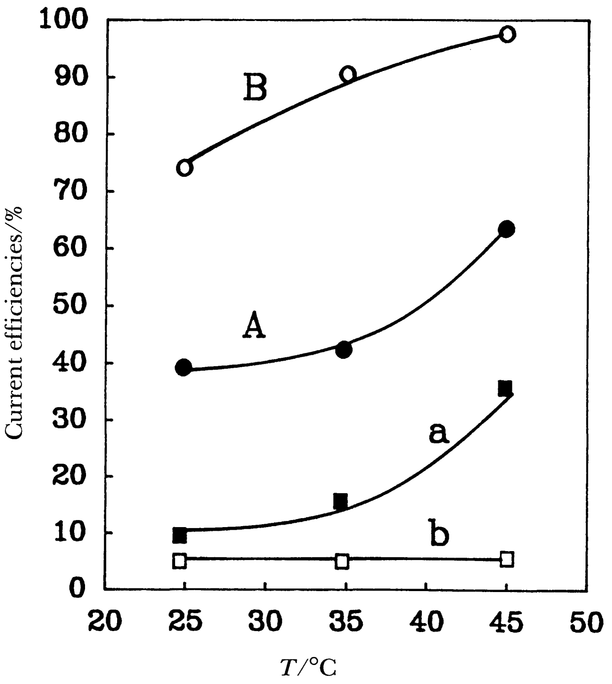

Fig. 5. Dependencies of current efficiencies on electrolysis temperature at 1.5 mA cm^{-2}. Mediator: PbO_2 (A and a), MnO_2 (B and b). Cinnamaldehyde (A and B), cinnamic acid (a and b).

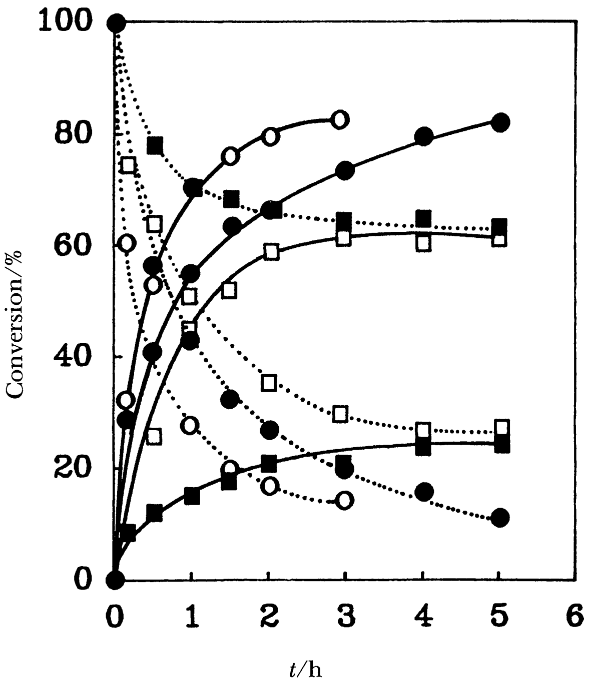

Fig. 6. Oxidation of cinnamyl alcohol by MnO_2 in neat THF (○), acetone (●), benzene (□), and acetic acid (■) at 22 °C. (——): cinnamaldehyde, (------): remaining cinnamyl alcohol.

reported that the half-wave potential for the oxidation of cinnamyl alcohol to cinnamaldehyde was 1.36 V, and that of cinnamaldehyde to cinnamic acid 1.77 V (vs. Ag/0.1 mol dm^{-3} Ag^+) in a CH_3CN-$NaClO_4$ solution system.[1,2] The potential difference between two oxidation steps is about 0.4 V. The above-mentioned potential values can not be directly compared with those in the present system since the electrodes, solvents, and reference electrodes are different. However, judging from the results described above, MnO_2 can oxidize the cinnamyl alcohol to cinnamaldehyde, but can not do so to cinnamic acid. On the other hand, the oxidation potential of PbO_2 is more positive by ca. 0.2 V than that of MnO_2, and it is sufficiently high to oxidize the alcohol to acid.

Chemical Reactions. The electrochemical oxidation of cinnamyl alcohol proceeds via consecutive reactions: electrochemical formation of oxides (Eqs. 1 and 2) is followed by their reaction with alcohol (Eqs. 3 and 4). It is not clear yet which of the reaction steps is rate-determining. We have examined the activation energy of anodic oxidation using Mn,Pt-Nafion. The value was 12.1 kcal mol^{-1}, higher than the value for the anodic formation of MnO_2 from Mn^{2+} on Pt (9.2 kcal mol^{-1}).[14] This result suggests that the reaction step of Eq. 3 or 4 is slower than the electrode reaction and following chemical reactions seem to be important in the mediatory systems. From this point of view, the chemical reactions of the oxides with cinnamyl alcohol were examined.

For electrochemical systems, THF was selected as a solvent, which was stable and did not remarkably swell Nafion. Some solvents were examined for possible use as a solvent for the chemical oxidation of cinnamyl alcohol by MnO_2. As shown in Fig. 6, THF gave the highest oxidation rate among the solvents examined. In all cases using neat solvents, no other product beside cinnamaldehyde was detected during HPLC analysis, while in electrochemical reaction systems acetone gave some unidentified by-products together with cinnamic acid. Since the reaction rate in THF was too high to examine the reaction in detail, acetone was selected as a solvent for the chemical oxidation.

The oxidation of cinnamyl alcohol by PbO_2 was examined in neat acetone. As shown in Fig. 7, the oxidation rate was faster than that by MnO_2. While only a trace amount of cinnamic acid was formed at 25 °C, a significant amount of the acid was formed at 40 °C.

The influence of the water content and acidity is easily inferred from Eqs. 1 to 4.[8] The influence of the water content on the oxidation is exhibited in Fig. 8. The reaction rate decreased with an increase in the water content, since the oxidation potential decreased with increasing water content, as can be expected from Eqs. 1 and 2. In the presence of water cinnamic acid was formed.

$$C_6H_5CH{=}CHCHO + MnO_2 + H_2O = C_6H_5CH{=}CHCOOH + Mn(OH)_2 \qquad (5)$$

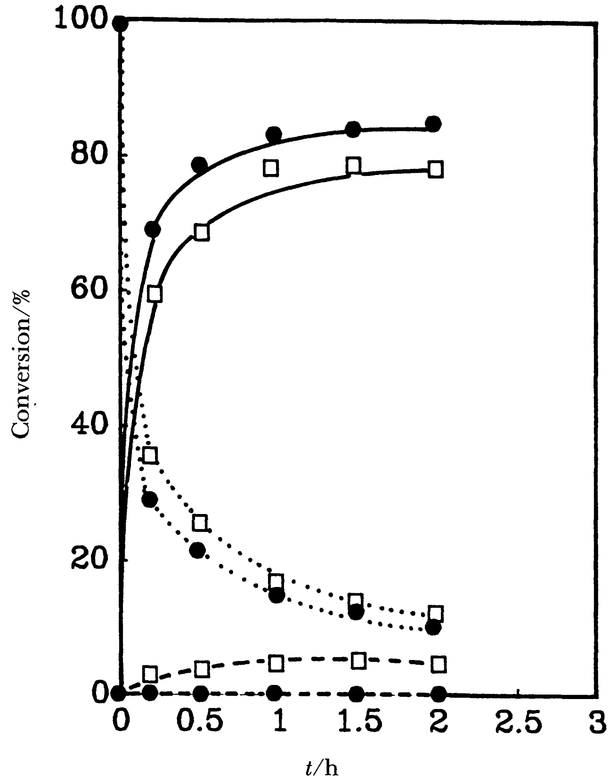

Fig. 7. Oxidation of cinnamyl alcohol by PbO_2 in neat acetone at 25 °C (●) and 40 °C (□). (——): cinnamaldehyde, (----): cinnamic acid, (·······): remaining cinnamyl alcohol.

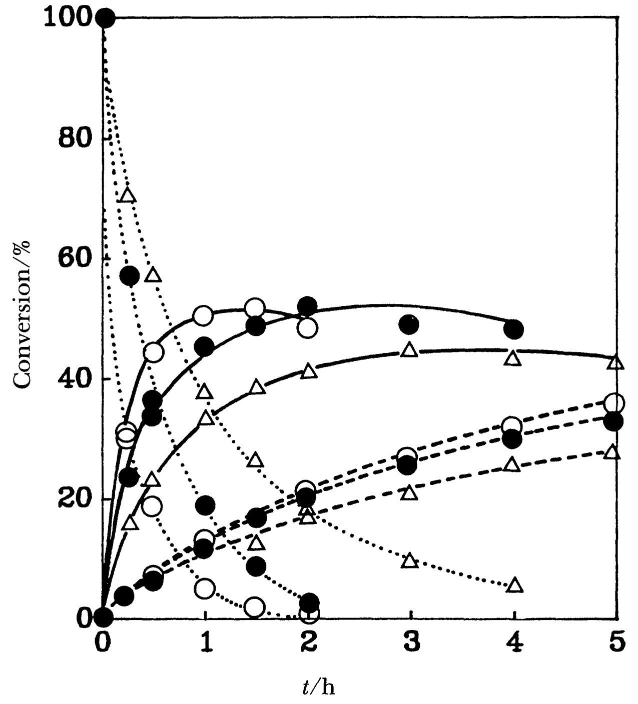

Fig. 8. Influence of water content in acetone on the oxidation of cinnamyl alcohol by MnO_2 at 22 °C. (·······): remaining alcohol, (——): cinnamaldehyde, (----): cinnamic acid. Water content: ○: 4%, ●: 6%, △: 8%.

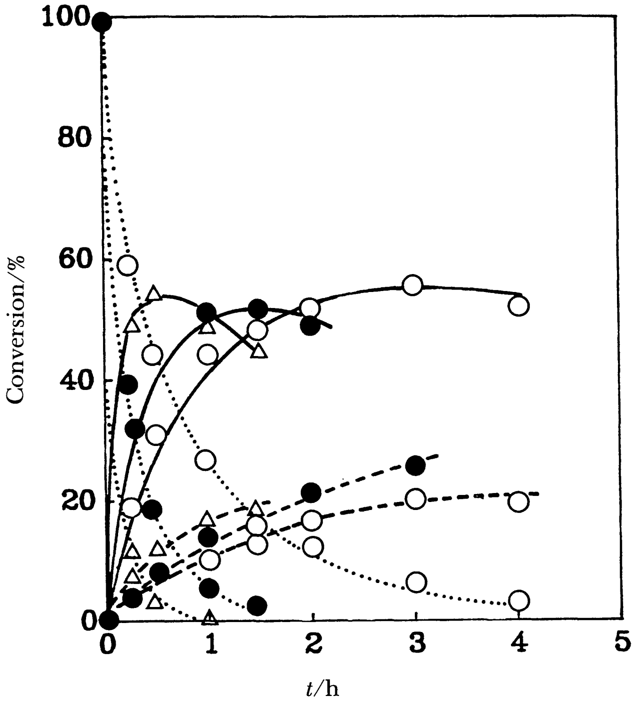

Fig. 9. Dependencies of conversion on sulfuric acidic concentration in acetone containing 4% of water by MnO_2 at 22 °C. (·······): remaining alcohol, (——): cinnamaldehyde, (----): cinnamic acid. H_2SO_4 (mol dm^{-3}), △: 0.65, ●: 0.43, ○: 0.22.

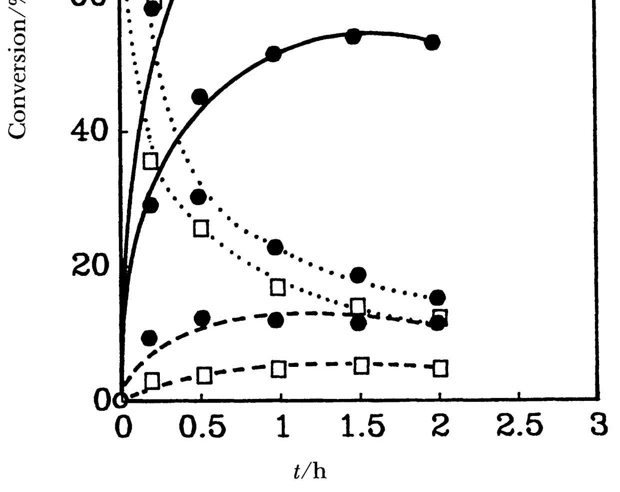

Fig. 10. Reactions of cinnamyl alcohol with PbO_2 at 40 °C in acetone containing 4% water and 0.43 mol dm^{-3} H_2SO_4 (●) and in neat acetone (□). (·······): remaining alcohol, (——): cinnamaldehyde, (----): cinnamic acid.

In the absence of water the aldehyde can not be oxidized by MnO_2. The decrease in acid formation upon increasing the water content can also be ascribed to a decrease in the oxidation potential. These results suggest the existence of an optimum water content.

An increase in the sulfuric acid concentration at a fixed water content of 4% increased the reaction rate as well as acid formation, as shown in Fig. 9. It is easily deduced from Eqs. 1 and 2 that an increase in acidity enhances the oxidation potential of MnO_2, and that this high oxidation potential enhances the reaction rate and acid formation.

Similar influences of the acid concentration were observed in the oxidation of cinnamyl alcohol by PbO_2. As is shown in Fig. 10, its oxidation rate was increased by the addition of sulfuric acid. However, this increase was due to its oxidation to cinnamic acid, and even a slight decrease in the current efficiency of the aldehyde formation was observed. Thereafter, the reaction selectivity to the aldehyde was decreased.

An increase in the acid concentration also accelerates the reaction rate of Eq. 3. The increased oxidation potential of oxides with an increase in a solution acidity, as well as the increased oxidation rate of Eq. 3, additively enhance the oxidation rate, though the contribution from the former seems to be larger at the low acid concentration examined here than that from the latter.

As expected, the increase in the reaction temperature enhanced the reaction rate of both aldehyde and acid formation, as shown in Fig. 11.

Figure 12 shows the difference between MnO_2 and PbO_2 in acetone at 40 °C. PbO_2 gave a greater oxidation rate than did MnO_2. Although cinnamic acid was not formed using MnO_2 (Fig. 6), it was formed using PbO_2. The higher oxidation potential of PbO_2 than MnO_2 explains the results.

It is not easy to determine the conditions surrounding an active site of Pt-Nafion, since Nafion is a strong acid-type cation-exchange membrane and its acidity is considered to correspond to 1—3 mol dm^{-3} H_2SO_4 under aqueous conditions. At the reaction site for the present mediatory electrochemical oxidation, a solvent, THF, is mixed with water, both of which exist in WEC and CEC, respectively. This mixing makes substrate transportation to the reaction site easy.[8] Although the acidity might be decreased by mixing, it may be considered that the reaction site on Pt-Nafion is an aqueous mixture and is fairly acidic. Under these conditions oxidation of the alcohol by two oxides must be rapid enough to supply M^{2+} ions to the electrode by the regeneration reaction (Eq. 3). The critical current density, above which the regeneration rate of Mn^{2+} can not follow up its consumption by a charge-transfer reaction on the anode, was about 2 mA cm^{-2}; this value was dependent on many factors, such as deposition conditions of platinum, the amount of metal oxide incorporated into Pt-

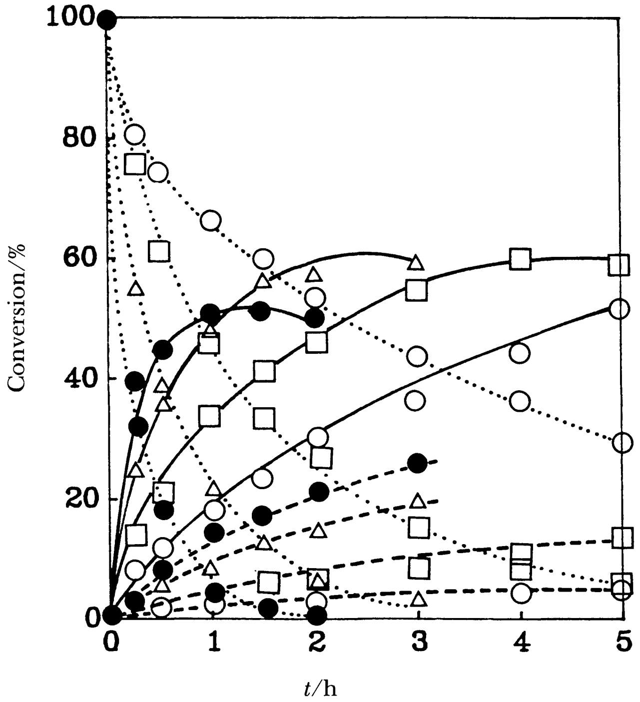

Fig. 11. Influence of temperature on conversion in acetone containing 4% water and 0.43 mol dm^{-3} H_2SO_4 by MnO_2.
(·······): remaining alcohol, (——): cinnamaldehyde, (----): cinnamic acid formation.
Temperature (°C): ○: 10, □: 20, △: 30, ●: 40.

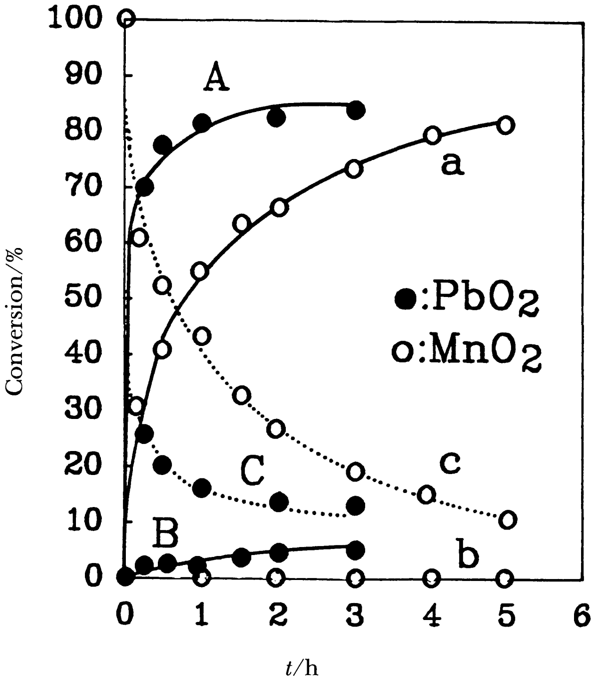

Fig. 12. Oxidation of cinnamyl alcohol in neat acetone by PbO_2 (A, B, C) and MnO_2 (a, b, c) at 40 °C. A and a: cinnamaldehyde, B and b: cinnamic acid, C and c: remaining cinnamyl alcohol.

Nafion, solvent composition, and temperature.

The results obtained for the mediatory electrochemical oxidation, that cinnamic acid production is more remarkable on Pb,Pt-Nafion than that on Mn,Pt-Nafion, were coincident with the results obtained through chemical oxidation.

References

1) N. L. Weinberg, "Technique of Electroorganic Synthesis," ed by N.L. Weinberg, John Wiley, New York (1974), Part II, pp. 733.

2) H. Lund, *Acta Chem. Scand.*, **11**, 491 (1957).

3) T. Shono, Y. Matsumura, J. Hayashi, and M. Mizoguchi, *Tetrahedron Lett.*, **2**, 1658 (1979).

4) S. Torii, T. Inokuchi, and T. Sugiura, *J. Org. Chem.*, **51**, 161 (1986).

5) T. Shono, Y. Matsumura, M. Mizoguchi, and J. Hayashi, *Tetrahedron Lett.*, **40**, 3861 (1979).

6) T. Shono, Y. Matsumura, J. Hayashi, and M. Mizoguchi, *Tetrahedron Lett.*, **21**, 1867 (1980).

7) Z. Ogumi, T. Mizoe, Z. Chen, and Z. Takehara, *Bull. Chem. Soc. Jpn.*, **63**, 3365 (1990).

8) Z. Chen, Z. Ogumi, T. Mizoe, and Z. Takehara, *Bull. Chem. Soc. Jpn.*, **64**, 537 (1991).

9) Z. Ogumi and Z. Takehara, *Denki Kagaku,* **52**, 70 (1984).

10) Z. Ogumi, H. Yamashita, K. Nishio, Z. Takehara, and S. Yoshizawa, *Denki Kagaku,* **52**, 180 (1984).

11) R. Adams and R.A. Wankel, *J. Am. Chem. Soc.*, **73**, 2219 (1951).

12) R. Kuhn and I. Hammer, *Chem. Ber.*, **83**, 413 (1950).

13) R. S. Yeo and H. L. Yeager, "Modern Aspect of Electrochemistry," ed by B. E. Conway, R. E. White, and J. O'M. Bockris, Plenum, New York (1985), Vol. 16, pp. 437.

14) M. Sugimori and T. Sekine, *Denki Kagaku,* **37**, 63 (1969).