Bull. Chem. Soc. Jpn., *58*, *201—206 (1985)*

Electrochemical Conversion of 2,3-Butanediol to Acetaldehyde by Oxidative Cleavage by a Periodate/Iodate Redox Mediatory System

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(Received July 30, 1984)

As electrochemical method was developed for converting 2,3-butanediol in dilute aqueous solutions to acetaldehyde by "in-cell" indirect anodic oxidation using a periodate/iodate redox mediatory system. Under optimum conditions, current efficiency for the desired acetaldehyde was close to 80% and the formation of by-products such as acetic acid, acetoin, and biacetyl was minimized or suppressed.

As part of a broad program pursued here and elsewhere whose main thrust is to explore the possibilites of converting electrochemically biomass-derived materials to (a) fuels or fuel components and/or (b) commercial organic chemicals, we have used 2,3-butanediol as a feedstock. Our results on the electrochemical conversion of this 1,2-diol to 2-butene (category *a* above)[1] and 2-butanone(category *b*)[2] had been reported; this paper concerns the conversion of the diol to acetaldehyde by electrooxidative cleavage.

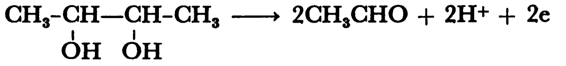
It is well known that 1,2-diols,including 2,3-butanediol, can be cleaved with oxidizing reagents such as chromium(VI) oxide, peroxodisulfates, lead(IV) tetraacetate, diacetoxyiodobenzene and periodates to give two moles of the corresponding carbonyl compounds in a variety of yields and selectivities.[3,4] 1,2-Diols give also the carbonyl compounds by electrooxidation under a variety of electrolytic conditions.[5—14] The electrochemical method for the oxidative cleavage of the diols may be generally favorable from the point of view of avoiding the use of large amounts of expensive, poisonous and/or hazardous reagents. In this regard, we examined the electrochemical oxidation of 2,3-butanediol to acetaldehyde.

2,3-Butanediol is obtained as dilute aqueous solutions whose concentrations are lower than 10%, usually a few percent, by the fermentation of glucose and xylose.[15—18] Therefore, the electrolytic method suitable for such dilute solutions should be recommended, though the crude solutions from the fermentation can be concentrated by distillation; pure 2,3-butanediol is obtainable with considerable difficulty.[19,20]

In this work, either direct or indirect(using a redox mediator) electrooxidation of 2,3-butanediol to acetaldehyde in dilute (mainly *ca.* 1%) aqueous solutions was examined and it was found that the indirect oxidation using the periodate/iodate redox mediator resulted in high current efficiencies and selectivities for acetaldehyde.

Results and Discussion

Horányi *et al.*[21,22] reported that 2,3-butanediol was oxidized directly at a platinized platinum anode in a strongly acidic solution to give acetoin and biacetyl. In this oxidation, however, no cleaved products such as acetaldehyde and acetic acid were formed. In this work, the direct oxidation (Eq. 1) was first examined by using anodes other than platinized platinum in strongly acidic, neutral and strongly alkaline solutions. Electrolyses were carried out in a divided cell. Although acetaldehyde was formed in the direct oxidation, its current efficiency and selectivity were very low under a variety of conditions used. Even in the best case where a lead(IV) dioxide anode was used in a neutral solution, considerably large amounts of by-products such as acetic acid (15% current efficiency), acetoin(17%) and biacetyl(3%) were formed along with the desired acetaldehyde(24%).



$$\underset{\mathrm{OH}}{\mathrm{CH_3\text{-}CH}}\text{—}\underset{\mathrm{OH}}{\mathrm{CH\text{-}CH_3}} \longrightarrow 2\mathrm{CH_3CHO} + 2\mathrm{H^+} + 2\mathrm{e} \qquad (1)$$

At the next stage of the investigation, the indirect oxidation using a suitable redox mediator was examined. Generally, either "in-cell" or "ex-cell" method may be available for indirect electrochemical oxidation and reduction. In this work, the "in-cell" method was favored, since it should be simpler in the whole system of electrolytic process.

As summarized by Torii,[23] a variety of organic and inorganic redox systems are available for indirect electro-oxidation of organic compounds. In this work, a periodate/iodate redox system was chosen as an electron-mediator, since 1,2-diols can generally cleaved by periodate oxidation to give the corresponding carbonyl compounds[3,4] and periodates are industrially produced by the electrochemical oxidation of iodates at lead(IV) dioxide anodes.[24—26] In addition, it has been confirmed by independent experiments that both periodates and iodates can not oxidize acetaldehyde. The indirect oxidation of 2,3-butanediol is pres-

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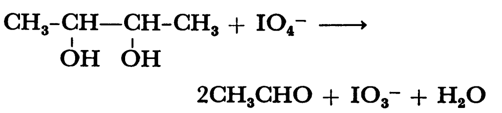
ented by Eqs. 2 and 3.

At anode:

$$IO_3^- + 2OH^- \longrightarrow IO_4^- + H_2O + 2e \qquad (2)$$

In solution:



$$\underset{\textstyle OH}{CH_3\text{-}CH}\text{—}\underset{\textstyle OH}{CH}\text{-}CH_3 + IO_4^- \longrightarrow 2CH_3CHO + IO_3^- + H_2O \qquad (3)$$

The pH dependence of the chemical oxidation of 2,3-butanediol to acetaldehyde was first examined. As shown in Fig. 1, yields of acetaldehyde were high at pHs higher than 6, though no examination was carried out in alkaline solutions because in the latter case condensation reactions of aldehyde occur.

On the other hand, as shown in Fig. 2, current efficiencies for periodate formed in the electrooxidation of iodate at a lead(IV) dioxide anode were high at pHs lower than 6.

From these facts, it seemed to be difficult to obtain both the highest yield of acetaldehyde and the highest current efficiency for periodate at the same pH. It was expected that the best result in actual electrolysis of 2,3-butanediol in sodium iodate solutions would be obtained in a range of pH 5—7. As shown in Fig. 3, the current efficiency for acetaldehyde formed in the indirect electrochemical oxidation of 2,3-butanediol at the lead(IV) dioxide anode in phosphate buffer solutions containing sodium iodate was at a high level close to 80% at pH 5—9. The current efficiency was somewhat affected by anodic potentials and the highest value was obtained at 2.00 V *vs.* SCE.

Decrease of the current efficiency at lower pHs, shown in Fig. 3, might be due to unfavorable oxidation of 2,3-butanediol to by-products with anodically generated periodate(Eq. 2) since the oxidation proceeded more disadvantageously at such pHs, as shown in Fig. 1. However, no by-product was formed in the chemical oxidation with sodium periodate at such pHs. This fact suggests that the decrease of the current efficiency for acetaldehyde may be due to occurrence of electrochemical side reactions to form products other

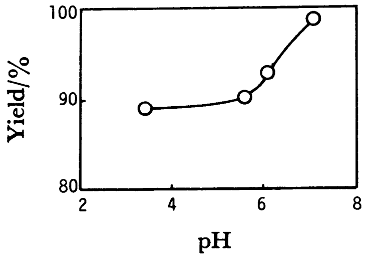


Fig. 1. pH-Dependence of Yield of Acetaldehyde Formed in the Chemical Oxidation of 2,3-Butanediol with Sodium Periodate.

2,3-Butanediol concentration, 0.1 M; Sodium periodate concentration, 0.2 M; Temperature, 40 °C; Reaction time, 20 s.

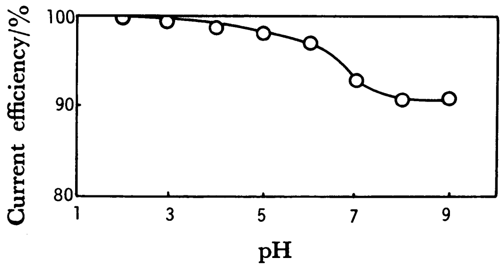


Fig. 2. pH-Dependence of Current Efficiency for Periodate Formed in the Electrochemical Oxidation of Sodium Iodate at a Lead Dioxide Anode.

Sodium iodate concentration, 0.2 M; Temperature, 38 °C; Anodic potential, 2.00 V *vs.* SCE

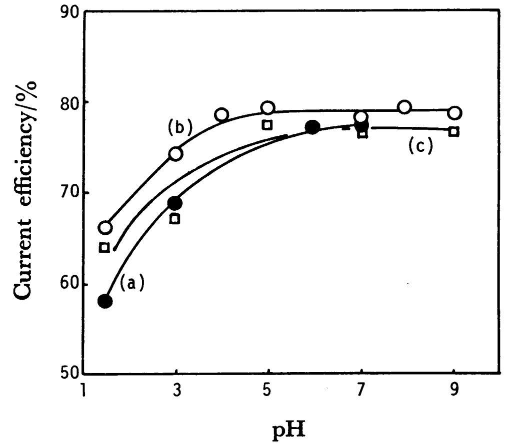


Fig. 3. pH-Dependence of Current Efficiency for Acetaldehyde Formed in the Indirect Electrochemical Oxidation of 2,3-Butanediol with a Periodate/Iodate Mediator at a Lead Dioxide Anode.

2,3-Butanediol concentration, 0.1 M; Sodium iodate concentration, 0.2 M; Temperature, 37 °C; Anodic potential, (a) 1.80 V *vs.* SCE, (b) 2.00 V, (c) 2.30 V; Charge passed, 0.67 F mol^{-1}.

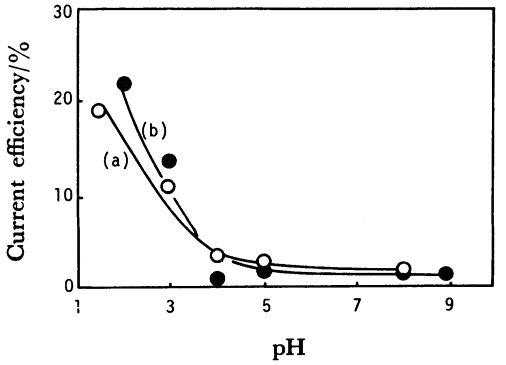


Fig. 4. pH-Dependence of Current Efficiencies for (a) Acetic Acid and (b) Acetoin Formed in the Indirect Electrochemical Oxidation of 2,3-Butanediol with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode.

2,3-Butanediol concentration, 0.1 M; Sodium iodate concentration, 0.2 M; Temperature, 37 °C; Charge passed, 0.67 F mol^{-1}; Anodic potential, 2.00 V *vs.* SCE.

than acetaldehyde. As shown in Fig. 4, the oxidation at the lower pHs provided larger amounts of by-products such as acetic acid and acetoin, while no biacetyl was formed at all pHs used. The oxidation potential of iodate seemed to be close to that of 2,3-butanediol (See Fig. 5) and the main products in the direct oxidation at the lead dioxide anode in the strongly acidic solution were acetic acid and acetoin. From these facts, the formation of the by-products at the lower pHs may be rationalized as due to the simultaneous direct oxidation with the indirect oxidation by electrogenerated periodate.

As shown in Fig.6 the highest current efficiency for acetaldehyde was obtained at 37 °C. Lower current efficiencies at higher temperatures might be partially due to loss of acetaldehyde by its evaporation.

The current efficiency for acetaldehyde was affected by the concentration of sodium iodate, as shown in Fig. 7. Lower efficiencies at lower concentrations may be due to simultaneous occurrence of the indirect and direct oxidation of 2,3-butanediol, the latter of which gave acetaldehyde in lower efficiencies. The direct oxidation should be relatively favorable at low concentration of sodium iodate, since the oxidation potential of 2,3-butanediol is not so far from that of sodium iodate even in a neutral solution (See Fig. 5). From the results in Fig. 7, concentrations higher than 0.2 M (1 M=1 mol dm^{-3}) should be desirable, but those higher than 0.3 M can not be actually used because of the limited solubility of sodium iodate in the electrolytic solution.

Curve(a) in Fig. 8 indicates that the current efficiency decreased with increase of concentration of 2,3-butanediol, when 0.67 F (1 F=96496 C) mol^{-1} of charge, which is proportional to the concentration, was passed. In such a manner of electrolysis, the ano-

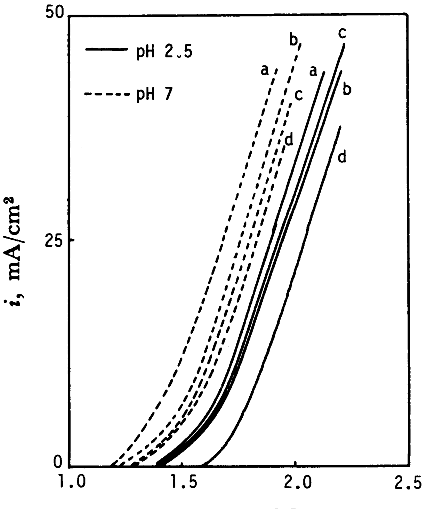


Fig. 5. *i-E* Curves at 37 °C and a Lead Dioxide Anode. (a): 0.2 M $NaIO_3$, (b): 0.1 M 2,3-Butanediol, (c): 0.08 M Acetaldehyde, (d): Background.

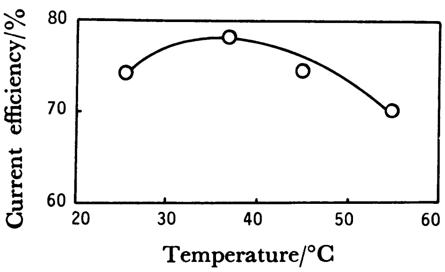


Fig. 6. Temperature-dependence of Current Efficiency for Acetaldehyde Formed in the Indirect Electrochemical Oxidation of 2,3-Butanediol with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode.
2,3-Butanediol concentration, 0.1 M; Sodium iodate concentration, 0.2 M; pH, 7; Anodic potential, 2.00 V *vs.* SCE; Charge passed, 0.67 F mol^{-1}.

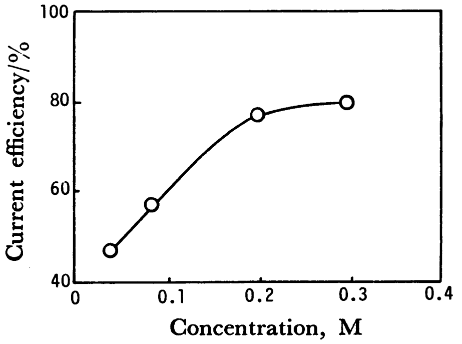


Fig. 7. Sodium Periodate Concentration-Dependence of Current Efficiency for Acetaldehyde Formed in the Indirect Electrochemical Oxidation of 2,3-Butanediol with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode.
2,3-Butanediol concentration, 0.1 M; pH, 7; Temperature, 37 °C; Anodic potential, 2.00 V *vs.* SCE; Charge passed, 0.67 F mol^{-1}.

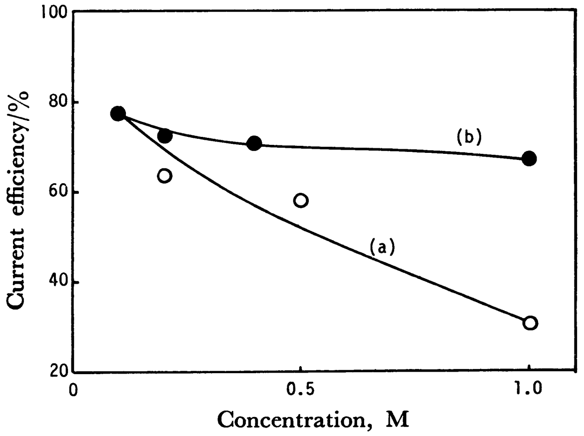


Fig. 8. 2,3-Butanediol Concentration-Dependence of Current Efficiency for Acetaldehyde Formed in the Indirect Electrochemical Oxidation of 2,3-Butanediol with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode.
Sodium iodate concentration, 0.2 M; pH, 7; Temperature, 37 °C; Anodic potential, 2.00 V *vs.* SCE; Charge passed, (a) 0.67 F mol^{-1} and (b) 0.0033 F for each concentration of 2,3-butanediol.

lyte should be acidified by the acid electrogenerated when large amounts of charge was passed at high concentration of 2,3-butanediol. In fact, after 0.67 F mol^{-1} (0.033 F for 50 mmol of 2,3-butanediol) was passed in 1.0 M 2,3-butanediol concentration, the pH decreased to 2.5 because of the insufficient buffering capacity of a phosphate solution used as the anolyte. Low current efficiency in this case also may be rationalized as due to simultaneous direct oxidation.

Curve(b) in Fig. 8 shows the results obtained by passing the same amount of charge(0.0033 F) at all the concentrations. In this case, a much smaller decrease of the current efficiency with increase of the concentration was observed, because the change of pH should be almost the same in each electrolysis.

From the above consideration, pH control is desired to obtain high current efficiencies, when such large amounts of charge are passed that high conversions of the starting 2,3-butanediol can be obtained when it is present in high concentrations. This point was further confirmed by Fig. 9. When large amounts of charge of 2.6 F mol^{-1} were passed without any pH control (to obtain almost 100% conversion), the current efficiencies for acetaldehyde and acetic acid were decreased and increased, respectively, as shown in Fig. 9.

Figure 9 also showes a result which was obtained by adjusting pH in the range of 7—6 by occasional addition of alkali during the electrolysis. Compared with the previous case, the result was improved.

When 2.5 F mol^{-1} of charge were passed in a high concentration (0.5 M, *ca.* 5%) of 2,3-butanediol under no pH control, the current efficiency for the desired acetaldehyde was lower than that for the by-product (acetic acid) as shown in Fig. 10. In this case, two more

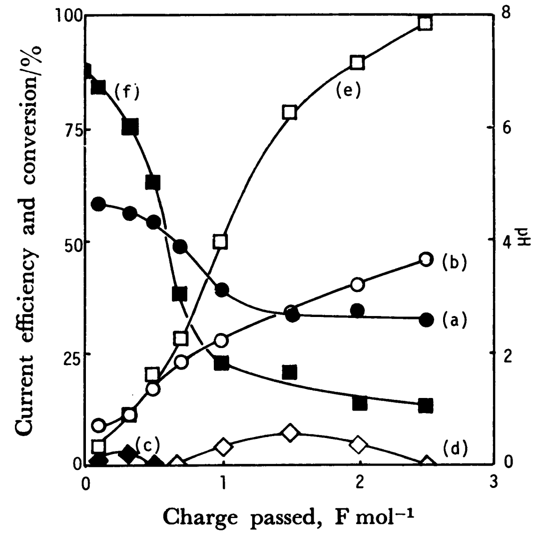


Fig. 10. Current Efficiencies for (a) Acetaldehyde, (b) Acetic Acid, (c) Acetoin and (d) Cyclic Acetal of 2,3-Butanediol, Conversion (e) of 2,3-Butanediol, and pH (f) in the Indirect Electrochemical Oxidation with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode.

2,3-Butanediol concentration 0.5 M (*ca.* 5%); Sodium iodate concentration, 0.2 M; Initial pH, 7 (not controlled); Anodic potential, 2.00 V *vs.* SCE; Temperature, 37 °C.

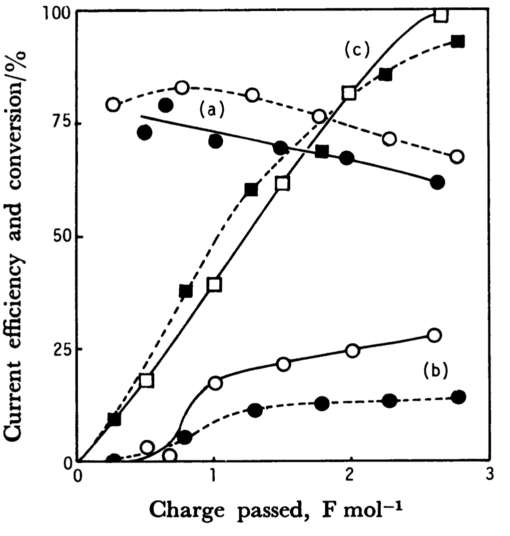


Fig. 9. Current Efficiencies for (a) Actealdehyde and (b) Acetic Acid, and Conversion (c) of 2,3-Butanediol in the Indirect Electrochemical Oxidation with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode: pH; ——, not controlled. ----, controlled at 7—6 by adding disodium hydrogenphosphate during the electrolysis.

2,3-Butanediol concentration, 0.1 M (*ca.* 1%); Sodium iodate concentration, 0.2 M; Initial pH, 7; Anodic potential, 2.00 V *vs.* SCE; Temperature, 37 °C.

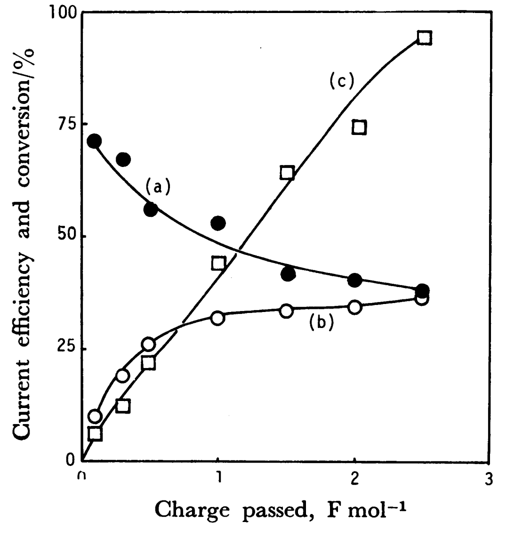


Fig. 11. Current Efficiency for (a) Acetaldehyde and (b) Acetic Acid, and Conversion (c) of 2,3-Butanediol in the Indirect Electrochemical Oxidation with a Periodate/Iodate Redox Mediator at a Lead Dioxide Anode.

2,3-Butanediol concenrtation, 0.5 M (*ca.* 5%); Sodium iodate concentration, 0.2 M; Initial pH, 7 (controlled at 7—6 by adding disodium hydrogenphosphate during the electrolysis); Anodic potential; 2.00 V. *vs.* SCE; Temperature, 37 °C.

by-products, acetoin and cyclic acetal of 2,3-butanediol(2,4,5-trimethyl-1,3-dioxolane), rose and fell in the course of the electrolysis. The pH control resulted in some improvements in the current efficiencies as shown in Fig. 11, but they were not satisfactory.

Acetaldehyde can not be oxidized with periodate, as described above, but it may be oxidized at an anode. In fact, acetaldehyde (0.48 M) was oxidized to acetic acid in 96% conversion and 78% current efficiency at 2.00 V *vs.* SCE (at lead(IV) dioxide anode) in a phosphate-buffered solution(pH 7) containing sodium iodate (0.2 M). Therefore, the decrease and increase of acetaldehyde and acetic acid, respectively, at high conversion of 2,3-butanediol is rationalized as due to the further oxidation of the former to the latter. To prevent the further oxidation, it should be effective to remove acetaldehyde from the anolyte by a suitable way during the electrolysis. This is a chemical engineering problem with which this paper is not concerned.

As described above, it was important to keep the pH in a suitable range and pH control was done by adding alkali to the anolyte during the electrolysis. There may be another way for the pH control, that is, the use of an undivided cell, which can be constructed more simply than divided ones. We attempted electrolyses in an undivided cell using a platinum cathode and lead(IV) dioxide anode, but good results could not be obtained because of the cathodic reduction of iodate to iodide (which was re-oxidized to iodine at the anode).

Conclusion

An optimization of the electrochemical conversion of 2,3-butanediol to acetaldehyde was established as follow: Electrolytic method, indirect oxidation; mediatory system, periodate/iodate redox; cell, divided; anode, lead(IV) dioxide; anodic potential, 2.00 V *vs.* SCE; pH, 7—6; temperature, 37 °C; concentration of sodium iodate, >0.2 M; concentration of 2,3-butanediol, several percent.

It is also recommended to remove acetaldehyde during the electrolysis so that it does not accumulate in the anolyte. For this purpose, continuous distillation and/or extraction may be available. If an efficient procedure for removing acetaldehyde is established, an "ex-cell" method for the indirect oxidation may become practicable, though it has not been established whether the "ex-cell" method is superior to the "in-cell" one.

Experimental

Materials. 2,3-Butanediol and lead(IV) dioxide anodes were supplied from Tokyo Kasei Kogyo Co. Ltd. and Sanwa Chemical Co. Ltd., respectively.

Electrolysis. An H-type divided cell with a sintered glass diaphragm and a potentiostat were used for controlled-potential electrolyses. Anodes were platinum (2.0×3.0 cm), lead(IV) dioxide (2.5×3.0 cm) and graphite (2.5×3.0 cm) plates. The direct oxidation of 2,3-butanediol was carried out in 0.5 M H_2SO_4, 1 M Na_2SO_4, and 1 M KOH, while anolytes for the indirect oxidation were phosphate-buffered solutions containing sodium iodate; 0.3 M Na_2HPO_4 (pH 9), Na_2HPO_4–NaH_2PO_4 (pH 8—4.5), 0.3 M Na_2HPO_4–0.5 M H_3PO_4 (pH 3), and NaH_2PO_4–H_2SO_4 (pH<3). Fifty mililiters of anolyte were used for each electrolysis.

Analysis. Starting 2,3-butanediol and all the products were analyzed by gas chromatography (1.5 m Chromosorb 101 column at 80—180 °C). Periodate was analyzed by the Fluery-Lange method.[22]

We are grateful to the Kajima Foundation for making possible Professor Chou's participation.

References

1) T. Nonaka and M. M. Baizer, *Electrochim. Acta,* **28**, 661 (1983).

2) M. M. Baizer, T. Nonaka, K. Park, Y. Saito, and K. Nobe, *J. Appl. Electrochem.,* **14**, 197 (1984).

3) Y. Ogata, "Yukikagobutsu no Sanka to Kangen (Oxidation and Reduction of Organic Compounds)," Nankodo, Tokyo, pp. 191, 248, 321, 343, 352 (1964).

4) H. O. House, "Modern Synthetic Chemistry," 2nd. Ed., W. A. Benjamin Inc., Monlo Park, p. 353 (1972).

5) A. Renard, *Ann. Chem.,* **17**, 313 (1879).

6) C. Neuberg, *Biochem. Z.,* **17**, 270 (1909).

7) W. Löb and G. Pulvermacher, *Biochem. Z.,* **17**, 343 (1909).

8) W. Löb and G. Pulvermacher, *Z. Elektrochem.,* **16**, 5 (1910).

9) E. Müller, *Z. Elektrochem.,* **27**. 565 (1921).

10) E. Tommila, *Ann. Acad. Sci. Fenn.,* **39**, 11 (1934).

11) T. Shono, Y. Matsumura, T. Hashimoto, K. Hibino, H. Hamaguchi, and T Aoki, *J. Am. Chem. Soc.,* **97**, 2546 (1975).

12) T. Shono, H. Hamaguchi, Y. Matsumura, and K. Yoshida, *Tetrahedron Lett.,* **1977**, 3625.

13) A. Yoshiyama, T. Goto, and T. Sekine, *J. Electrochem. Soc. Jpn.,* **49**, 532 (1981).

14) T. Fuchigami, T. Nonaka, C. Watanabe, A. Yoshiyama and T. Sekine, *J. Electrochem. Soc. Jpn.,* **51**, 812 (1983).

15) G. A. Adams and R. Y. Stanier, *Can. J. Res.,* **23B**, 1 (1945).

16) A. C. Blackwood, A. C. Neish, W. E. Brown, and G. A. Ledingham, *Can. J. Res.,* **25B**, 56 (1947).

17) A. C. Neish, A. C. Blackwood, F. M. Robertson, and G. A. Ledingham, *Can. J. Res.,* **25B**, 65 (1947).

18) A. C. Neish, A. C. Blackwood, F. M. Robertson, and G. A. Ledingham, *Can. J. Res.,* **26B**, 335 (1948).

19) A. C. Neish, *Can. J. Res.,* **23B**, 10 (1945).

20) D. Rose and W. S. King, *Can. J. Res.,* **23F**, 79 (1945).

21) G. Horányi, G. Inzelt and K. Torkos, *J. Electroanal. Chem. Interfacial Electrochem,* **106**, 305 (1980).

22) G. Horányi and G. Inzetl, *Ann. Univ. Sci. Budapestinensis de Rolando Eötvös Nominatase, Sec, Chim.,* **1980**, 47.

23) S. Torii, "Yukidenkaigosei (Organic Electrosyntheses)," Kodansha, Tokyo, p. 303 (1981).

24) H. H. Willard, and R. R. Ralston, *J. Electrochem. Soc.*, **62**, 239 (1932).

25) C. L. Mehltretter and C. S. Wise, *Ind. Eng. Chem.*, **51**, 511 (1959).

26) Y. Aiya, S. Fujii, K. Sugino and K. Shirai, *J. Electrochem. Soc.*, **109**, 419 (1962).

27) E. L. Fleury and J. Lange, *J. Pharm. Chem.*, **17**, 107, (1933).