

SHORT COMMUNICATION

Paired electrooxidation**Part III: Production of *n*-butyric acid from *n*-butanol**

Y.-L. CHEN, T.-C. CHOU*

Department of Chemical Engineering, National Chung Kung University, Tainan, Taiwan, Republic of China, 701

Received 14 August 1995; revised 14 September 1995

1. Introduction

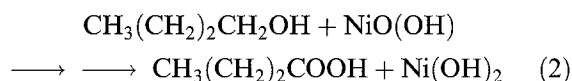
It is well known that, except for methanol and benzyl alcohol, alcohol oxidation is not easy in the absence of a redox mediator since direct oxidation of alcohols at platinum and carbon anodes is limited because of the requirement of high oxidation potentials. In earlier work, nickel in aqueous potassium hydroxide was used as the anode to cause the oxidation of primary alcohol to form carboxylic acid in current yields in excess of 90% [1]. Nickel oxide hydroxide NiO(OH), is continuously produced by the electrooxidation of nickel hydroxide. The application of NiO(OH), prepared by chemical methods, to alcohol oxidation has been well studied [2–4]. Recently, a nickel hydroxide electrode was used for alcohol oxidation through indirect electrochemical oxidation [1, 5–10]. Many papers have reported that the oxidation of alcohol has both high current efficiency and yield using a nickel or nickel hydroxide plated electrode as anode. However, when oxidation takes place in such a system, the current at the cathode does not contribute to the electrolysis process. Therefore, paired electrolysis is examined in this study with a view to increasing the total current efficiency. In paired electrolysis, hydrogen peroxide is produced at the cathode to oxidize the reactant, here *n*-butanol. Thus, oxidation occurs at both anode and cathode. Several papers have reported the idea of paired electrolysis [11, 12]. In these papers, oxidation did not occur by direct electrooxidation at the cathode but required indirect oxidation through redox mediators, such as, Mn³⁺/Mn²⁺, V⁵⁺/V⁴⁺, Ce³⁺/Ce²⁺, S₂O₈²⁻/SO₄²⁻. These redox mediators are expensive and require separation from the electrolyte. Some authors have carried out cathodic reduction of oxygen to produce hydrogen peroxide [13–16]. Some papers have reported using H₂O₂ combined with metallic redox mediators for cathodic oxidation [17, 18]. But paired electrolysis by simultaneous oxidation through peroxide compounds generated both at anode and cathode has not been reported. In this study, the combination of anodic and direct cathodic oxidation without redox mediators was carried out and paired electrolysis was examined at different controlled current values in divided and undivided cells. Though *n*-butanol cannot be easily oxidized, very high current efficiency was obtained. The reactions in the paired electrochemical

oxidation of *n*-butanol to *n*-butyric acid may be expressed as follows.

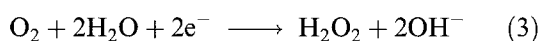
Anodic reaction [8–10]:



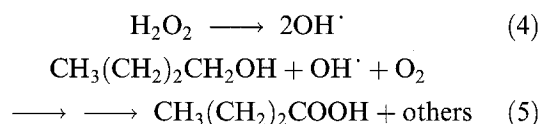
Chemical reaction in anodic compartment by NiO(OH) as oxidation agent:



Cathodic reactions:



Chemical reactions in cathodic compartment by both H₂O₂ and O₂ as oxidation agents:



Oxidation mechanisms by peroxide compounds at both anode and cathode are also examined in detail.

2. Experimental details

Nickel electrode was polished with fine emery paper and then washed with 0.5 M nitric acid followed by washing with distilled water. The d.c. current was supplied by an EG&G 273A potentiostat/galvanostat with a 270 electrochemical analysis system. All potentials are quoted relative to the reference electrode, Ag/AgCl/saturated KCl aqueous solution prepared in house. When paired electrolysis was carried out, a flow of oxygen, of 3 ml s⁻¹ was purged into the reactor. The controlled current electrolysis was performed in a divided or an undivided cell. The products of electrolysis were analyzed using a Varian 3300 gas chromatograph with a DB-1 capillary. The samples were injected into a DB-1 capillary. The column, injector and detector temperatures were 180, 200 and 250 °C, respectively.

3. Results and discussion**3.1. Current efficiencies for *n*-butanol oxidation in the paired electrolysis**

The gas chromatographic analysis revealed that the only detectable product was *n*-butyric acid in the

* Author to whom correspondence should be addressed.

Table 1. Effect of current density on current efficiency for *n*-butyric acid in a divided cell

Anode, 6 cm² nickel; cathode, 21 cm² graphite; electrolyte solution, 1.0 M KOH containing 0.1 M *n*-butanol; charge passed, 0.6 Faraday mol⁻¹ *n*-butanol; oxygen purge rate, 3 ml s⁻¹; agitation rate, 700 rpm.

Current/mA	Current density/mA cm ⁻²		CE/%		
	Anode	Cathode	Anode	Cathode	Total
10*	1.67	0.71	86.9	84.9	171.9
10	1.67	0.48	86.1	89.0	175.2
15	2.50	0.71	83.0	85.3	168.3
20	3.33	0.95	70.1	70.7	140.8
30	5.00	1.43	43.0	30.1	73.2
40	6.67	1.90	32.0	14.4	46.4

* Cathode: 14 cm² graphite.

paired electrolysis of *n*-butanol in both divided and undivided cells. The other possible oxidation product, *n*-butyl aldehyde was not found, as shown in Tables 1 and 2. To obtain the best current efficiency for *n*-butyric acid at anode and cathode, the desired current density at anode and cathode can be adjusted by changing the surface area of the electrodes. As shown in Table 1, when 10 mA was applied, the cathodic current efficiencies of *n*-butyric acid were 84.9 and 89.0% for areas of 14 and 21 cm², respectively. This indicates that the higher the current density, the lower the current efficiency for H₂O₂. The amount of *n*-butyric acid is proportional to the amount of H₂O₂ produced at the cathode. Thus, low current density is preferred; at the cathode, oxygen is reduced to hydrogen peroxide at low current density but to water at high current density [13, 14, 19, 20]. In Do and Chen's study [13, 14], the best current density using graphite as cathode to produce the highest current efficiency of H₂O₂ is about 0.5 mA cm⁻². At the anode, the extent of water decomposition increases when the current density increases [9, 10]. Thus, the higher the current density, the lower the current efficiencies in both anolyte and catholyte. As shown in Table 1, increasing the anodic current density from 1.67 to 6.67 mA cm⁻², reduces the current efficiency from 86.1 to 32.0%, and increasing the cathodic current density from 0.48 to 1.90 mA cm⁻², reduces the

Table 2. Effect of current density on current efficiency for *n*-butyric acid in an undivided cell

Anode, 6 cm² nickel; cathode, 21 cm² graphite; electrolyte solution, 1.0 M KOH containing 0.1 M *n*-butanol; charge passed, 0.6 Faraday mol⁻¹ *n*-butanol; oxygen purge rate, 3 ml s⁻¹; agitation rate, 700 rpm.

Current/mA	Current density/mA cm ⁻²		Total CE/%
	Anode	Cathode	
10	1.67	0.48	165.8
15	2.50	0.71	162.5
20	3.33	0.95	132.8
30	5.00	1.43	67.1
40	6.67	1.90	39.3

Table 3. Effect of current density on power consumption in divided and undivided cells

Anode, 6 cm² nickel; cathode, 21 cm² graphite; electrolyte solution, 1.0 M KOH containing 0.1 M *n*-butanol; charge passed, 0.6 Faraday mol⁻¹ *n*-butanol; oxygen purge rate, 3 ml s⁻¹; agitation rate, 700 rpm.

Current/mA	Current density/mA cm ⁻²		Power consumption/kWh mol ⁻¹ <i>n</i> -butyric acid			
	Anode	Cathode	Divided			Undivided
			Anode	Cathode	Total	Total
10*	1.67	0.71	0.26	0.27	0.13	—
10	1.67	0.48	0.26	0.25	0.13	0.07
15	2.50	0.71	0.29	0.28	0.14	0.10
20	3.33	0.95	0.35	0.35	0.18	0.15
30	5.00	1.43	0.65	0.93	0.38	0.31
40	6.67	1.90	1.02	2.26	0.83	0.37

* Cathode: 14 cm² graphite.

current efficiency from 89.0 to 14.4%. That is, the total current efficiency of the paired electrolysis reduces from 175.2 to 46.4% as the controlled current increases from 10 to 40 mA in a divided cell. The total current efficiency is over 100% when the current is lower than 30 mA in this system. Paired electrolysis was also carried out in an undivided cell as shown in Table 2. As the controlled current increased from 10 to 40 mA in the undivided cell, i.e., current density increased from 1.67 to 6.67 mA cm⁻² at the anode and from 0.48 to 1.90 mA cm⁻² at the cathode, the total current efficiency decreased from 165.8 to 39.3%. Both in the undivided cell and divided cell, low current density is preferred to achieve high current efficiency. The total current efficiencies in an undivided cell are almost equal to the total current efficiencies in a divided cell. The divided cell is not really necessary in such a paired electrolysis system. Paired electrolysis of *n*-butanol using an undivided cell is convenient in practical operation.

3.2. Power consumption for *n*-butanol oxidation in paired electrolysis

The power consumption per mole *n*-butyric acid in paired electrolysis using an undivided cell is lower than that using a divided cell. As shown in Table 3, the total power consumption increases from 0.13 to 0.83 kWh mol⁻¹ *n*-butyric acid as the current increases from 10 to 40 mA in the divided cell. However, the total power consumption increases from 0.07 to 0.37 kWh mol⁻¹ *n*-butyric acid as current increases from 10 to 40 mA in the undivided cell. The divided equipment causes increased cell voltage at the same current.

Acknowledgement

The support of the National Science Council for Republic of China (NSC 82-0405-E-006-420) and National Chung Kung University is acknowledged.

References

- [1] M. Fleischmann, K. Korinek and D. Pletcher, *J. Chem. Soc., Perkins Trans.* **2** (1972) 1396.
- [2] M. V. George and K. S. Balachandran, *Chem. Rev.* **75** (1975) 491.
- [3] R. Konaka, S. Terabe and K. Kuruma, *J. Org. Chem.* **34** (1969) 1334.
- [4] K. Nakagawa, R. Konaka and T. Nakata, *ibid.* **27** (1962) 1597.
- [5] M. Fleischmann, K. Korinek and D. Pletcher, *J. Electroanal. Chem.* **31** (1971) 39.
- [6] M. Amjad, D. Pletcher and C. Smith, *J. Electrochem. Soc.* **124** (1977) 203.
- [7] J. Kaulen and H. J. Schafer, *Tetrahedron* **38** (1982) 3299.
- [8] H. J. Schäfer, in 'Topics in Current Electrochemistry', vol. 142 (edited by E. Steckhan), Springer-Verlag, Berlin and New York (1987) pp. 101–108.
- [9] Y. L. Chen and T. C. Chou, submitted to *Electrochim. Acta*.
- [10] *Idem*, submitted to *I&EC Research*.
- [11] J. J. Jow, A. C. Lee and T. C. Chou, *J. Appl. Electrochem.* **17** (1987) 753.
- [12] A. C. Lee and T. C. Chou, *ibid.* **23** (1993) 1259.
- [13] J. S. Do and C. P. Chen, *J. Electrochem. Soc.* **140** (1993) 1632.
- [14] *Idem*, *I&EC Research* **33** (1994) 387.
- [15] S. Masao, K. Hisatsugu and K. Kozo, *J. Chem. Eng. Jpn* **18** (1985) 364.
- [16] S. Masao, K. Takamasa, H. Haruyoshi and S. Hiroshi, *J. Chem. Eng. Jpn.* **21** (1988) 198.
- [17] Y. L. Hsiao and K. Nobe, *J. Appl. Electrochem.* **23** (1993) 943.
- [18] M. Sudoh, T. Kodera, K. Sakai, J. Q. Zhang and K. Koide, *J. Chem. Eng. Jpn* **19** (1986) 513.
- [19] R. C. M. Jakobs, L. J. Janssen and E. Barendrecht, *Electrochim. Acta* **30** (1985) 1433.
- [20] I. Morcos and E. Yeager, *ibid.* **15** (1970) 953.