

Electrochemical reduction of benzaldehyde using Pt–Pb/Nafion[®] as electrode

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The electrochemical reduction of benzaldehyde using Pt–Pb/Nafion[®] as electrode without supporting electrolyte in the liquid organic phase was investigated. A novel Pt–Pb/Nafion[®] electrode was prepared for the electrolysis of the organic compound in this solid polymer electrolyte (SPE[®]) system. A reaction mechanism is proposed. No benzyl alcohol was produced using fresh Nafion[®] as electrode. The selectivity of benzyl alcohol using Pt–Pb/Nafion[®] as an electrode was almost 100% and only a trace of hydrobenzoin byproduct was found in the catholyte. The optimum faradic yield of benzyl alcohol was 18.70 g F⁻¹. The primary factors affecting the current efficiency or faradic yield of the cathodic reduction of benzaldehyde to benzyl alcohol were cell voltage, solvent and temperature. The use of a Pt–Pb/Nafion[®] electrode in a SPE[®] system for the electrochemical reduction of benzaldehyde was found to be a feasible technique.

1. Introduction

Choosing a suitable solvent and supporting electrolyte are key factors for successful electrochemical synthesis of organic compounds. The electrochemical synthesis of organic compounds is normally carried out in an aqueous solution with supporting electrolyte. The solubility of organic compounds in aqueous solution is, unfortunately, poor. In general, there are two phases in this electrolysis system. Mass transfer across the interface of this two-phase system is difficult. Suitable phase transfer catalyst [2–4], solvent and supporting electrolyte [5–7] in the organic phase are required for the two-phase electrolysis system. For both the aqueous and nonaqueous system, the addition of solvent makes the consumption of energy higher. The type of solvent may influence the selectivity of an electrochemical organic synthesis [8]. Besides, the addition of phase transfer catalyst, solvent and supporting electrolyte may also make the process more complicated and expensive and lead to separation problems. Several advantages arise in using the solid polymer electrolyte method for organic synthesis; for example, the system is simplified, no supporting electrolyte and solvent are required, pollution is reduced and product separation is easier.

A solid polymer electrolyte system has been applied in water electrolysis [9, 10] and fuel cells [11, 12]. In general, the metals embedded in the SPE[®] are noble metals, such as Pt, Ir, and Ru [8–13]. These electrodes are not always suitable materials when applied to electrochemical organic synthesis since the hydrogen overpotentials of some metals are comparatively lower [14]. Electrochemical syntheses using SPE[®]

electrodes have been previously investigated [15–19]. In special cases, mediators or modified electrodes are necessary to increase the current efficiency [15, 16]. The modified treatments make the electrolysis process more complicated, so the advantages are more or less suppressed. In this work, SPE[®] electrode, Pt–Pb/Nafion[®], with high hydrogen overpotential has been prepared and successfully applied to electrochemical organic syntheses. The cathodic reduction of benzaldehyde at a Pt–Pb/Nafion[®] electrode without the addition of solvent and liquid supporting electrolyte in benzaldehyde has been systematically studied. Those factors which affect the faradic yield or current efficiency have also been explored.

2. Experimental details

2.1. Pretreatment of SPE[®]

The SPE[®] membrane, Nafion[®] 117, was swollen in methanol for 1 h, boiled in 0.3 wt % H₂O₂ solution for 2 h, boiled in 5 N H₂SO₄ solution for another 2 h, and then washed in deionized distilled water several times for removal of those protons not tightly bounded or exchanged on the membranes. The pretreated membranes were finally kept in deionized distilled water.

2.2. Preparation of Pt–Pb/Nafion[®] using an electroless plating method

The pretreated SPE[®] was fixed in an acrylic cylinder as described previously [20]. At 40°C, a 5 ml 0.1 M lead nitrate solution was put into the cylinder. The Pb²⁺ ions exchanged with protons in the membrane

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for 2 h. The exchanged Pb²⁺ membrane was then washed in deionized distilled water. A 5 ml mixture of palladium chloride and hydrogen chloride solution (adding 0.25 g PdCl₂ and 2.5 ml concentrated HCl into 1 dm⁻³ water) was placed in the cylinder for 1 min at room temperature; then the membrane fixed in the cylinder was thoroughly washed in deionized distilled water. A mixture of 5 ml 0.4 wt % NaBH₄ and 0.4 wt % LiOH aqueous solution was introduced into the cylinder. The reduction reactions took place at 40 °C, and a uniform lead deposition layer gradually formed. The reduction process was completed after 20 min and the surface of the Pb/Nafion[®] was then washed in deionized distilled water. Following the above treatment, a mixture of a 2 ml 1.0 wt % hexachloroplatinic acid and a 3 ml 0.2 wt % hydrazinium dichloride solution was added to form a protection layer; the platinum on Pb/Nafion[®], so-called Pt-Pb/Nafion[®], was finally washed again and kept in deionized distilled water.

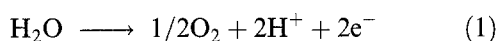
2.3. Reduction of benzaldehyde

The SPE[®] electrode system was set up as described previously [20]. The solution in the anodic chamber was 0.5 M H₂SO₄; the solution in the cathodic chamber was pure benzaldehyde. The anolyte and catholyte were circulated at a flow rate of 8 ml min⁻¹. During a run, the reaction was carried out at a set temperature within ±0.5 °C. The electrolysis solution was periodically sampled and analysed by a Varian 3300 gas chromatograph. The samples were injected into a DB-1 capillary, temperature programmed from 120 to 170 °C at 8 °C per minute, and with a 30 ml min⁻¹ nitrogen carrier gas.

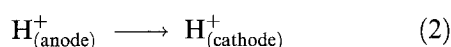
3. Results and discussion

3.1. Reaction mechanism and product analysis

The reaction mechanism for the cathodic reduction of benzaldehyde in the Pt-Pb/Nafion[®] system is schematically illustrated in Fig. 1, i.e. anodic reaction



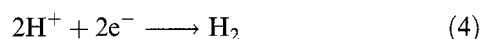
proton transfer



cathodic reaction



cathodic side reactions



The protons and electrons, which are produced by water electrolysis at the anode, can transfer through the membrane and the external circuit to the

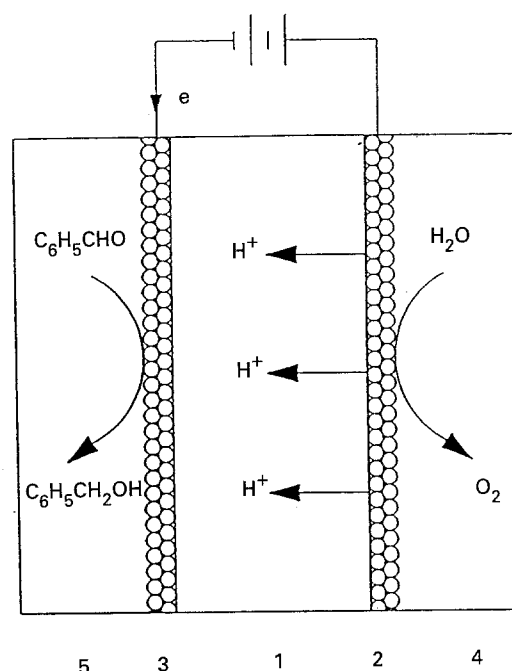


Fig. 1. Schematic representation of cathodic reduction of benzaldehyde. (1) Solid polymer electrolyte, (2) anode, (3) cathode, (4) anode chamber, (5) cathode chamber.

cathode, respectively. At the cathode, the protons and electrons reduce benzaldehyde to benzyl alcohol as shown in Equation 3. The protons transfer through the membrane to the cathode, so the proton concentration difference between membrane and embedded alloys is high. The high concentration of protons make the side reactions, Equations 4 and 5, possible. In particular, the production of hydrogen is much larger than that of hydrobenzoin. The selectivity of benzyl alcohol was almost 100%. The main reaction paths are Equations 3 and 4. The main catholyte products are benzaldehyde and benzyl alcohol, and only a trace of organic byproducts.

3.2. Effect of cell voltage

Using a Pt-Pb/Nafion[®] electrode, the current efficiency for benzyl alcohol production increases from 29.82 to 34.59% when the cell voltage increases from 3.0 to 6.0 V, as shown in Table 1 and Fig. 2. As

Table 1. Effect of cell voltage on current efficiency and faradic yield of benzyl alcohol

Cell voltage /V	Current efficiency/%		Faradic yield of benzyl alcohol /g(faraday) ⁻¹
	Benzyl alcohol	Hydrobenzoin	
3.0	29.82	trace	16.12
4.0	31.59	trace	17.27
5.0	32.80	trace	17.73
6.0	34.59	trace	18.70
7.0	33.23	trace	17.97
8.0	23.04	trace	12.46

Temperature: 25 °C, anolyte and catholyte flow rate: 8 ml min⁻¹; charge passed: 1000 C; anode: Pt, anode area: 10 cm²; anode chamber: 25 ml 0.5 M H₂SO₄; cathode: Pt-Pb/Nafion[®]; cathode area: 5 cm²; cathode chamber: reactant 10 ml pure ArCHO.

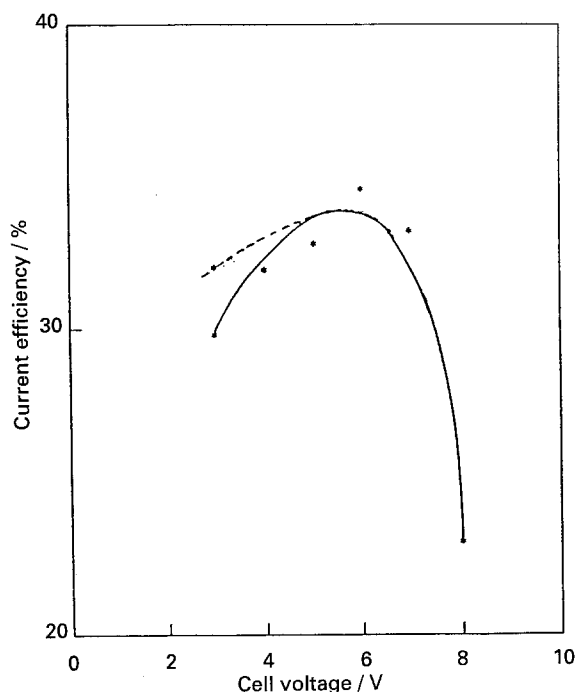


Fig. 2. Effect of cell voltage on current efficiency for benzyl alcohol production. Temperature: 25°C, anolyte and catholyte flow rate: 8 ml min⁻¹; charge passed: (—) 1000 C and (---) 500 C; anode Pt; anode area: 10 cm²; anode chamber: 25 ml 0.5 M H₂SO₄; cathode: Pt-Pb/Nafion®; cathode area: 5 cm²; cathode chamber: reactant; 10 ml pure ArCHO.

the cell voltage increases from 6.0 to 8.0 V, the current efficiency of benzyl alcohol decreases from 34.59 to 23.04%. The maximum current efficiency is 34.59% at 6.0 V. The hydrogen overvoltage is high in the range of high cell voltage, so hydrogen evolution increases with cell voltage. Accordingly, the current efficiency for benzyl alcohol decreases with cell voltage when the cell voltage is greater than 6.0 V. In the range of low cell voltage, increasing cell voltage increases the current efficiency. For a fixed amount of charge passed, decreasing the cell voltage increases the total time of electrolysis. Because the reaction time lengthens, the organic phase and aqueous phase become mixed in the reaction zone. When the concentration of reactant reduces, the current efficiency of benzyl alcohol decreases. In confirming this finding, the reaction time was shortened to only 500 C and the current efficiency increased from 29.82% to 32.03% at 3.0 V.

3.3. Effect of solvent

The current efficiency and faradic yield depend on both the type and the initial concentration of solvent, as indicated in Table 2 and Fig. 3. Using tetrahydrofuran (THF) as solvent, increasing the initial concentration of benzaldehyde from 4.9 to 8.9 M either increases the current efficiency of benzyl alcohol from 20.38 to 34.02% or increases the faradic yield from 11.02 to 18.32 g(faraday)⁻¹. Both the current efficiency and faradic yield are lowered more seriously using benzene as solvent than when using THF. Increasing the initial

Table 2. Effect of solvent on current efficiency and faradic yield of benzyl alcohol

Solvent	ArCHO conc. /M	Current efficiency of benzyl alcohol /%	Faradic yield of benzyl alcohol /g(faraday) ⁻¹
No	9.8	34.59	18.70
THF	8.9	34.02	18.38
THF	6.5	28.76	15.55
THF	4.9	20.38	11.01
Benzene	8.9	30.29	16.38
Benzene	6.5	23.07	12.47
Benzene	4.9	17.18	9.29

Temperature: 25°C, anolyte and catholyte flow rate: 8 ml min⁻¹; charge passed: 1000 C; cell voltage: 6.0 V; anode: Pt; anode area: 10 cm²; anode chamber: 25 ml 0.5 M H₂SO₄; cathode: Pt-Pb/Nafion®; cathode area: 5 cm²; cathode chamber: ArCHO organic solution.

benzaldehyde concentration in benzene from 4.9 to 8.9 M increases the current efficiency from 17.18 to 30.29% and the faradic yield from 9.29 to 16.38 g(faraday)⁻¹. The effect of solvent on the current efficiency for benzyl alcohol depend on both the structure of the SPE® and the transfer of species within the SPE®. The structure of Nafion® 117 can be divided into hydrophobic and hydrophilic regions. The deposited metal primarily disperses in the hydrophilic region since the SPE® electrodes are prepared by an ion-exchange method, and the process of ion-exchange chiefly proceeds in the region where sulfonic ions cluster together. Two solvents, benzene and THF, of different solubilities in water, were introduced to the electrolysis system to examine this phenomenon. The solubilities of benzene and

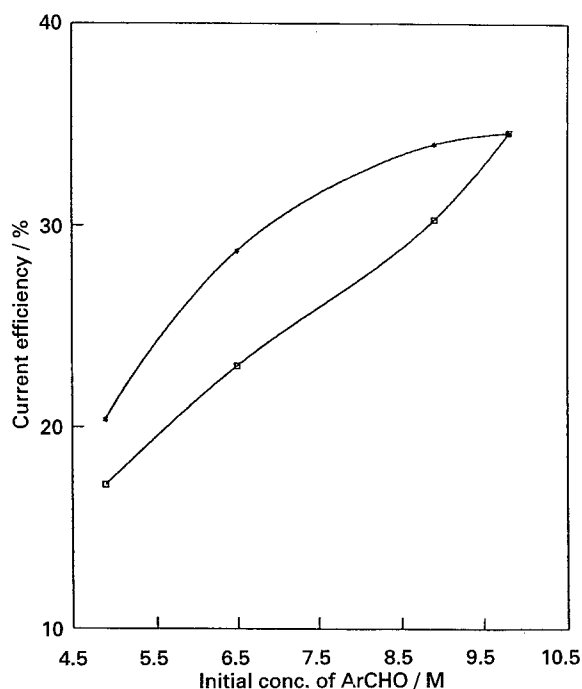


Fig. 3. Effect of solvent on current efficiency for benzyl alcohol production. Temperature: 25°C; anolyte and catholyte flow rate: 8 ml min⁻¹; charge passed: 1000 C; cell voltage: 6.0 V; anode: Pt; anode area: 10 cm²; anode chamber: 25 ml 0.5 M H₂SO₄; cathode: Pt-Pb/Nafion®; cathode area: 5 cm²; cathode chamber: ArCHO organic solution. (*) THF, (□) benzene.

THF are 0.178 g per 100 g water and infinite, respectively. Theoretically, the organic reactant cannot arrive at the hydrophilic reaction zone effectively. THF drags the reactant to the hydrophilic reaction zone and, consequently, increases the current efficiency for benzyl alcohol. However, benzene decreases the concentration of reactant only. Consequently, it results in low current efficiency. The results revealed that, using THF as solvent, the reduction in the current efficiency for benzyl alcohol was not as significant as when using benzene as a solvent. Two contradictory effects arise when using THF as solvent in a SPE® system; one promotes the transfer of the reactant to the hydrophilic reaction zone, and the other reduces the concentration of reactant. Based on the results of using THF as a solvent, the effect of decreasing reactant concentration is much more significant than that of promoting the transfer rate of reactant to the hydrophilic reaction zone. Since the solubility of benzene in water is low, benzene does not promote the transfer of organic reactant to the hydrophilic reaction zone but rather only decreases the concentration of the organic reactant. The current efficiency decrease using benzene as solvent is more significant than that using THF as solvent. However, solvents of high solubility in water for electrochemical organic synthesis in a SPE® system have been reported in the literature, e.g. the anodic oxidation of cinnamyl alcohol using THF as solvent, and the cathodic reduction of nitrobenzene using methanol as solvent [22, 23]. Solvent of high solubility in water could increase the current efficiency in these two systems. Some results of [22, 23] were different from the results of this study. Based on the present experimental results, the promotion of transfer of reactant by solvent THF is less significant than the effect of dilution of the reactant concentration in the reaction zone.

3.4. Effect of temperature

As shown in Table 3 and Fig. 4, both the current efficiency and faradic yield are significantly affected by temperature. When the temperature increases from 25 to 40°C, the current efficiency decreases from 34.59 to 25.42%, and the faradic yield decreases from 18.70 to 13.74 g (faraday)⁻¹, as shown

Table 3. Effect of temperature on current efficiency and faradic yield of benzyl alcohol

Temperature /° C	Current efficiency of benzyl alcohol /%	Faradic yield of benzyl alcohol /g (faraday) ⁻¹
25	34.59	18.70
30	28.63	15.48
40	25.42	13.47

Cell voltage: 6.0 V, anolyte and catholyte flow rate: 8 ml min⁻¹; charge passed: 1000 C; anode: Pt; anode area: 10 cm²; anode chamber: 25 ml 0.5 M H₂SO₄; cathode: Pt-Pb/Nafion®; cathode area: 5 cm²; cathode chamber: reactant 10 ml pure ArCHO.

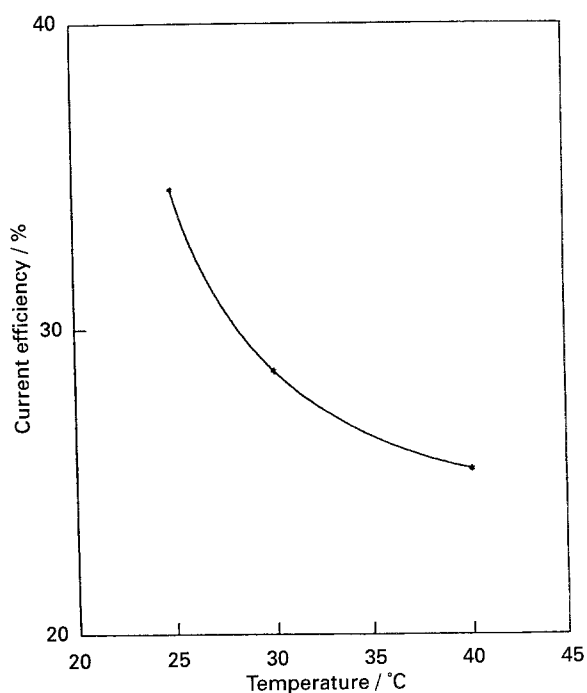


Fig. 4. Effect of temperature on current efficiency for benzyl alcohol production. Cell voltage: 6.0 V; anolyte and catholyte flow rate: 8 ml min⁻¹; charge passed: 1000 C; anode: Pt; anode area: 10 cm²; anode chamber: 25 ml 0.5 M H₂SO₄; cathode: Pt-Pb/Nafion®; cathode area: 5 cm²; cathode chamber: reactant; 10 ml pure ArCHO.

in Table 3. In general, the reaction rate increases with temperature. However, both the swelling and mixing effects of organic and aqueous phases of this electrolysis system increase with temperature. The extent of water electrolysis increases with temperature at the reaction zone and the current efficiency for benzyl alcohol production decreases.

Acknowledgement

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