

## Paired electrosyntheses using thin layer flow cell

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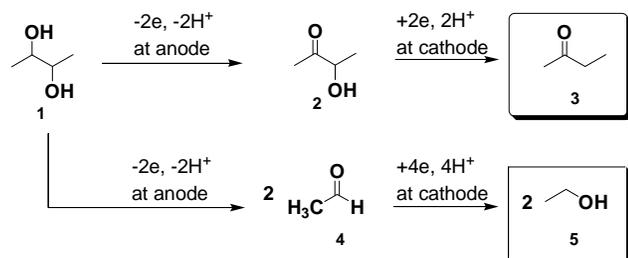
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### INTRODUCTION

Organic electrosynthesis is a powerful tool for organic synthesis, however a large amount of supporting electrolyte must be added to the solvent to give electrical conductivity, which might cause its separation problem from the reaction mixture in work up. To resolve this problem, Marken and coworkers have demonstrated that by using a micro-flow cell with coupled diffusion layers between electrodes, two electron-two proton reaction of tetraethyl ethylenetetraacboxylate in ethanol was realized without the electrolyte.<sup>1)</sup>

Meanwhile, paired electrosynthesis processes have been known as a practical and convenient methodology for some types of bulk electrolyses.<sup>2-4)</sup> One type of paired electrosynthesis is a process forming the same product from the same starting compound at the cathode and anode can theoretically give 200% current efficiency for the product. Therefore, it is expected the application of the above paired electrosynthesis by using thin layer flow cell in which the two diffusion layers of working and auxiliary electrodes overlap or become ‘coupled’.

In this work, we attempted to use a thin layer flow cell with 80  $\mu$  m in thickness for paid electrosynthesis of 2-butanone (**3**) and ethanol (**5**) from 2,3-butanediol (**1**) (Scheme 1).



Scheme 1

### EXPERIMENTAL

The thin layer flow cell was constructed by Pt or PbO<sub>2</sub> anode and Pb cathode (1 cm width, 3 cm length). A spacer (both side adhesive tape, 80  $\mu$  m thickness) was used to leave a rectangular channel exposed, and sandwiching the two electrodes together (Figure 1). After connecting Teflon tube to inlet and outlet, the cell was sealed with epoxy resin. The flow rate of reaction solution was controlled by using plunger pump. Electrolysis of 2,3-butanediol (3 mM) was carried out in constant current using ion exchange water as a reaction medium in the presence and absence of a supporting electrolyte, and products were analyzed by gas chromatography.

### RESULTS AND DISCUSSION

At first, the flow rate effect on the paired electrosynthesis in a Pt / Pb flow cell or a PbO<sub>2</sub> / Pb flow cell was investigated by using ion exchange water / 0.5 M Na<sub>2</sub>SO<sub>4</sub>, respectively. As shown in Tables 1 and 2, the total yield was found to be slightly higher at Pt anode than at PbO<sub>2</sub> anode.

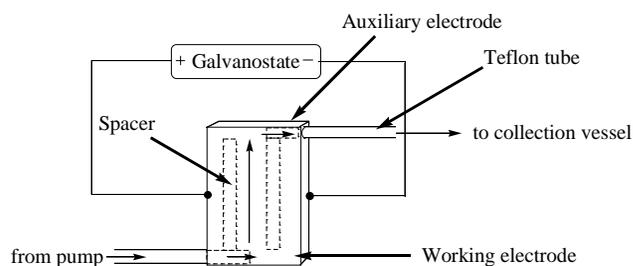


Figure 1. Schematic representation of thin layer flow cell for electrochemical reaction.

Table 1. Paired electrosynthesis of 2-butanone and ethanol from 2,3-butanediol using Pb cathode and PbO<sub>2</sub> anode

| Entry | Current | Flow rate   | Yield* |       |       | Conversion(%) |
|-------|---------|-------------|--------|-------|-------|---------------|
|       |         |             | 2 (%)  | 3 (%) | 5 (%) |               |
| 1     | 45 mA   | 0.01 ml/min | trace  | 1     | 2     | 97            |
| 2     | 45 mA   | 0.02 ml/min | trace  | 1     | 0.5   | 94            |
| 3     | 45 mA   | 0.03 ml/min | trace  | 5     | 2     | 81            |
| 4     | 45 mA   | 0.05 ml/min | 2      | 2     | 2     | 80            |

Supporting electrolyte: Na<sub>2</sub>SO<sub>4</sub> (0.5 M). Concentration of SM : 3 mM. Electrode area: 1 × 3 cm<sup>2</sup>.

\* Yield was determined by GC.

Table 2. Paired electrosynthesis of 2-butanone and ethanol from 2,3-butanediol using Pb cathode and Pt anode

| Entry | Current | Flow rate   | Yield* |       |       | Conversion(%) |
|-------|---------|-------------|--------|-------|-------|---------------|
|       |         |             | 2 (%)  | 3 (%) | 5 (%) |               |
| 1     | 45 mA   | 0.01 ml/min | trace  | 3     | 1     | 96            |
| 2     | 45 mA   | 0.02 ml/min | 2      | 3     | 3     | 88            |
| 3     | 45 mA   | 0.03 ml/min | 2      | 5     | 4     | 85            |
| 4     | 45 mA   | 0.05 ml/min | 2      | 3     | 4     | 64            |

Supporting electrolyte: Na<sub>2</sub>SO<sub>4</sub> (0.5 M). Concentration of SM : 3 mM. Electrode area: 1 × 3 cm<sup>2</sup>.

\* Yield was determined by GC.

Subsequently, paired electrosynthesis experiments in the absence of the electrolyte were performed. The results are summarized in Table 3. It is found that the yield of ethanol (**5**) was increased comparing with that in Table 2. Further investigations to optimize reaction conditions and mechanistic aspects are now investigating.

Table 3. Paired electrosynthesis of 2-butanone and ethanol from 2,3-butanediol using Pb cathode and Pt anode without supporting electrolyte

| Entry | Current | Flow rate   | Yield* |       |       | Conversion(%) |
|-------|---------|-------------|--------|-------|-------|---------------|
|       |         |             | 2 (%)  | 3 (%) | 5 (%) |               |
| 1     | 45 mA   | 0.01 ml/min | trace  | 0     | 23    | 84            |
| 2     | 45 mA   | 0.02 ml/min | trace  | 0     | 30    | 85            |
| 3     | 45 mA   | 0.03 ml/min | trace  | trace | 25    | 74            |
| 4     | 45 mA   | 0.05 ml/min | trace  | 1     | 21    | 67            |

Supporting electrolyte: Non. Concentration of SM : 3 mM.

Electrode area: 1 × 3 cm<sup>2</sup>.

\* Yield was determined by GC.

### References

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