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Bipolar membrane electrodialysis in an organic medium: Production of methyl methoxyacetate

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ABSTRACT

To produce methyl methoxyacetate in a safe and environmentally friendly manner, bipolar membrane electrodialysis is proposed to convert methyl chloroacetate into methyl methoxyacetate in an organic medium—methanol. The results indicate that as current density increases, the product yield increases, but the current efficiency decreases. Besides, as methyl chloroacetate concentration increases, both the product yield and current efficiency increase; i.e., the product concentration increases from 1.08 to 6.59 mmol dm^{-3}, and the current efficiency increases from 2.6% to 15.7%.

1. Introduction

Methyl methoxyacetate is an intermediate often used for synthesis of vitamin B6 [1], optical resolution of amine compounds, catalysis on polymerization, etc. This intermediate is conventionally prepared from methyl chloroacetate and sodium methoxide [2] (Eq. (1)) according to the mechanism of "Williamson synthesis":

$$ClCH_2COOCH_3 + NaOCH_3 \rightarrow CH_3OCH_2COOCH_3 + NaCl \quad (1)$$

In this process, sodium methoxide is a raw material not only expensive but also difficult for storage (reacting with the H_2O in air). Its high cost is related to its preparation method: metathesis between sodium and methanol, or double decomposition of sodium hydroxide and methanol. The former reaction consumes an expensive metal (Na) and can be explosive and thus dangerous; the latter has a low productivity since the reactant methanol and the product H_2O will form an azeotrop and make it difficult to purify sodium methoxide. To overcome the shortcomings mentioned above, it is necessary to explore a safe technique to generate sodium methoxide in situ for preparation of methyl methoxyacetate.

Alcohol splitting in bipolar membrane electrodialysis (BMED) is such a technique. Bipolar membrane electrodialysis is an electrodialysis employing a special type of ion exchange membrane: bipolar membrane. A bipolar membrane comprises a cation-selective layer and an anion-selective layer, and its well-known function is to split water into OH^- and H^+ under reverse bias in a direct current field [3–6]. However, the bipolar membrane can also realize alcohol splitting; i.e., alcohol is split into alkoxide anions and H^+. Sridhar first reported methanol splitting in bipolar membranes [7] and successfully applied it to the production of acetoacetic ester [8].

In this work, an experimental study is carried out on the production of methyl methoxyacetate by running BMED in methanol with $LiNO_3$ as the supporting electrolyte and methyl chloroacetate as the raw material. The parameters that affect the process efficiency and product yield, such as methyl chloroacetate concentration, current density, and electrodialysis time, are discussed.

2. Experimental

2.1. Materials

A cation exchange membrane (Neosepta CMX, Tokuyama Soda Inc., Japan), an anion exchange membrane (FT-FAB, FuMA-Tech GmbH, Germany), and a bipolar membrane (Neosepta BP-1, Tokuyama Soda Inc., Japan) were used for experiments, and their properties are listed in Table 1. The chemicals were of analytical grade. Distilled water was used throughout.

2.2. Setup

According to our preliminary tests, the anode and mono-polar membranes suffered from oxidization by Cl_2 if a BMED stack of BP-A or BP-C configuration (BP, bipolar membrane; C, cation exchange

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Table 1
Main properties of the membranes used in the BMED stack.

Membrane	Thickness (μm)	IEC (mequiv. g^{-1})	Area resistance ($\Omega\,cm^2$)	Voltage drop (V)	Efficiency (%)
FT-FAB	120	0.8	2–4[a]	–	–
Neosepta CMX	140–200	1.5–1.8	2.0–3.5[b]	–	–
Neosepta BP-1	200	–	–	1.2–2.2[c]	>98[c]

[a] 0.6 mol dm^{-3} NaCl at 25 °C.
[b] 0.5 mol dm^{-3} NaCl at 25 °C.
[c] 1 mol dm^{-3} NaOH and 1 mol dm^{-3} HCl, 10 A dm^{-2}, 30 °C.

membrane; A, anion exchange membrane) was employed to convert $ClCH_2COOCH_3$ into $CH_3OCH_2COOCH_3$ in methanol. The Cl^- ions would transport into the anode chamber as the counter-ions across the anion exchange membrane (for BP-A configuration) or co-ions across the cation exchange membrane (for BP-C configuration), and Cl_2 will be released from the anode. Therefore, a BMED stack of BP-C-A configuration (Fig. 1), instead of BP-A or BP-C configuration, was chosen for laboratory-scale experiments. This stack was composed of a bipolar membrane, a cation exchange membrane, and an anion exchange membrane between two electrodes, and the electrodes were connected with a direct current power supply (N5772A, Agilent Technologies, Co., Ltd.). Chambers were separated by Plexiglas spacers (thickness = 1 cm), and the solution in each chamber was circulated separately by a submersible pump (AP1000, Zhongshan Zhenhua Electronics Co., Ltd., China). Specially, the effective membrane area was 7.07 cm^2 and the electrodes were made of titanium coated with ruthenium. 0.2 mol dm^{-3} $LiNO_3$ methanol solution (250 cm^3) was used as the supporting electrolyte in all chambers, and a certain amount of methyl methoxyacetate (0.1–0.8 mol dm^{-3}) was added to product chamber (between the cation exchange membrane and the bipolar membrane; Fig. 1). In the anode chamber (between the anode and the anion exchange membrane; Fig. 1), 2 cm^3 H_2O was added and thus the following reaction took place: $2H_2O \rightarrow 4H^+ + O_2\uparrow + 4e$; the cathode released hydrogen.

To monitor the change of voltage across the bipolar membrane, two platinum wires were placed on both sides of bipolar membrane (Fig. 2), and the voltage drop was measured by a digital multimeter.

Before each experiment, the equipment was dried and kept from moisture, and all the membranes were conditioned in a 0.2 mol dm^{-3} $LiNO_3$ methanol solution for 24 h at room temperature before mounted into the stack.

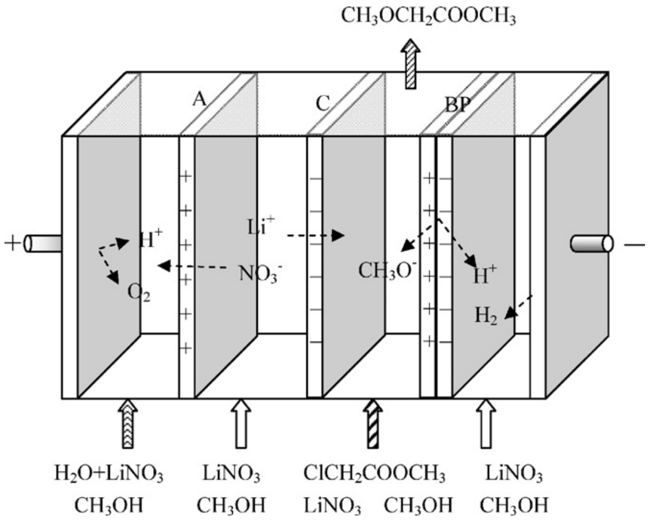

Fig. 1. Schematic of the experimental setup. BP, bipolar membrane; C, cation exchange membrane; A, anion exchange membrane.

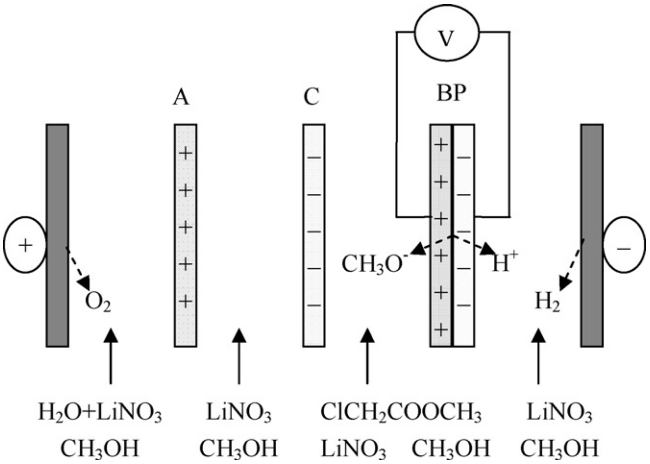

Fig. 2. Schematic of measuring the voltage drop across the bipolar membrane.

2.3. *Determination of methyl methoxyacetate and lithium methoxide*

The qualitative and quantitative analyses of methyl methoxyacetate were performed using a gas chromatograph (6890N, Agilent Technologies, Co., Ltd.). The concentration of lithium methoxide was determined by titration.

2.4. *Calculation of current efficiency*

The current efficiency η was calculated as Eq. (2) [9]:

$$\eta\,(\%) = \frac{(c_t - c_0)zVF}{It} \times 100 \qquad (2)$$

Where C_t and C_0 are the methoxide concentration at times t and 0, respectively, z is the ion chemical valence ($z = 1$), V is the circulate volume of solution in the base cycle, I is the current, and F is the Faraday constant. In this work, t is equal to 2 h, and the change of fluid volume in each cycle was negligible, that is, $V = 0.25$ L.

3. Results and discussion

3.1. *Voltage–time curves*

Fig. 3a illustrates the evolution of stack voltage drop at different current densities. Obviously, as current density increases, the voltage drop across the stack increases. When it comes to each curve, there is a sharp increase in the voltage drop at the beginning but a trend to level off afterwards. The sharp increases can have similar explanations as reported [10,11]: there is little current due to the increase in electrical resistance because ions are depleted in the intermediate layer of bipolar membrane. The stack voltage drop keeps approximately constant afterwards, indicating that the methanol dissociation at this condition approaches a steady state.

As shown in Fig. 3b, the stack voltage drop increases as methyl chloroacetate concentration increases from 0.1 to 0.8 mol dm^{-3}.