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Alcohol splitting for the production of methyl methoxyacetate: Integration of ion-exchange with bipolar membrane electrodialysis

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ABSTRACT

As a green technology for organic synthesis, alcohol splitting by using bipolar membrane electrodialysis (BMED) is restricted from industrial practice due to the unacceptable electrical resistance of the organic medium. This research proposes an integration strategy to reduce the electrical resistance, i.e., filling ion-exchange resins in a BMED stack. This strategy is adopted for the production of methyl methoxyacetate in methanol, and the performance of 4 kinds of ion-exchange resins are assessed in terms of the voltage drop, product yield, and current efficiency. Under the experimental conditions, the lowest voltage drop was achieved by using D201 macroreticular anion-exchange resin, and the voltage drop decreased by 44.3–61.4%. However, there was a slight decrease in the product yield and current efficiency due to the adsorption of methyl methoxyacetate onto the resins. As a compromise, 201*7 gel-type anion-exchange resin is the best choice.

1. Introduction

Water splitting ($H_2O \rightarrow H^+ + OH^-$ [inside a bipolar membrane]) is the typical function of bipolar membrane electrodialysis (BMED) and has been widely used in food processing, chemical synthesis, and environmental protection [1–4]. In comparison, alcohol splitting (Alcohol $\rightarrow H^+$ + Alkoxide anion [inside a bipolar membrane]) has much fewer reports, but it is of great significance to green organic industry because it can supply alkoxide anions in a safe and environmentally friendly manner and simplify many organic syntheses (e.g., Claisen condensation and intramolecular Dickman condensation) [5–10]. However, the first obstacle to the industrialization of alcohol splitting is the unacceptable energy consumption for running BMED in the organic medium (e.g., methanol and ethanol). Notably, alcohols, different from water, have much higher electrical resistances even after supporting electrolytes are added.

To further reduce the electrical resistance of alcohol, the general principal of EDI (electrodeionization) may be applied, i.e., adding ion-exchange resins in the solvent and making the resins a bridge to carry ions. Recently, this principal has achieved many successes in aqueous systems, such as producing high-purity water by CEDI (continuous electrodeionization) [11] and producing tartaric acid by adding strong acid resins in BMED [12].

This research will apply the principal of EDI to reduce the electrical resistance of an organic system, i.e., ion-exchange is integrated with BMED for alcohol splitting. In particular, methanol splitting in BMED is used to convert methyl chloroacetate into methyl methoxyacetate [9] (Eq. (1)), and 4 kinds of ion-exchange resins are filled in BMED, respectively. The effects of ion-exchange resins on the voltage drop, product yield, and current efficiency will be investigated.

$$ClCH_2COOCH_3 + CH_3O^- \rightarrow CH_3OCH_2COOCH_3 + Cl^- \quad (1)$$

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. D001 cation-exchange resins and D201 anion-exchange resins were supplied by Bengbu Tianxing Ion-exchange Resin Co., Ltd. (China). 001*7 and 201*7 resins were purchased from Sinopharm Chemical Reagent Co., Ltd. (China). The properties of the 4 kinds of ion-exchange resins are listed in Table 2. Before use, the resins were converted to the H^+ or OH^- form firstly, then immersed in methanol for 24 h, and filtrated under vacuum to remove methanol. The other chemicals were of analytical grade.

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Table 1
Properties of the membranes used in BMED stack.

Membrane	Type	Thickness (μm)	IEC (mequiv. g^{-1})	Area resistance (Ω cm^2)	Voltage drop (V)	Efficiency (%)
FT-FAB	Anion-exchange	120	0.8	2–4[a]	–	–
Neosepta CMX	Cation-exchange	140–200	1.5–1.8	2.0–3.5[b]	–	–
Neosepta BP-1	Bipolar	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.

Table 2
Properties of 4 ion-exchange resins.

Ion-exchange resins	Structure	Type	IEC (mequiv. g^{-1})	Water content (%)	Density (g mL^{-1})	Diameter (mm)
D001	Macroreticular	Cation-exchange; strongly acidic	4.35	45–55	1.25–1.28	0.315–1.25
D201	Macroreticular	Anion-exchange; strongly basic	4.0	50–60	1.06–1.11	0.315–1.25
001*7	Gel-type	Cation-exchange; strongly acidic	≥4.2	46–52	1.23–1.28	0.3–1.2
201*7	Gel-type	Anion-exchange; strongly basic	≥3.0	40–50	1.06–1.11	0.3–1.2

2.2. Setup

A BMED stack of BP-C-A configuration (Fig. 1) was chosen for laboratory-scale experiments, and ion-exchange resins were filled in the alkali compartment. 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.). Compartments were separated by Plexiglas spacers (thickness = 1 cm), and the solution in each compartment was circulated separately by a submersible pump (AP1000, Zhongshan Zhenhua Electronics Co., Ltd., China). The effective membrane area was 7.07 cm^2 and the electrodes were made of titanium coated with ruthenium. A methanol solution of $LiNO_3$ (0.2 mol dm^{-3}) was used as the supporting electrolyte in every compartment. 0.1 mol dm^{-3} $ClCH_2COOCH_3$ was used as the raw material for the production of methyl chloroacetate in all experiments. In the anode compartment, 2 cm^3 of H_2O was added and thus the following reaction took place: $2H_2O \rightarrow 4H^+ + O_2\uparrow + 4e$; the cathode released hydrogen.

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

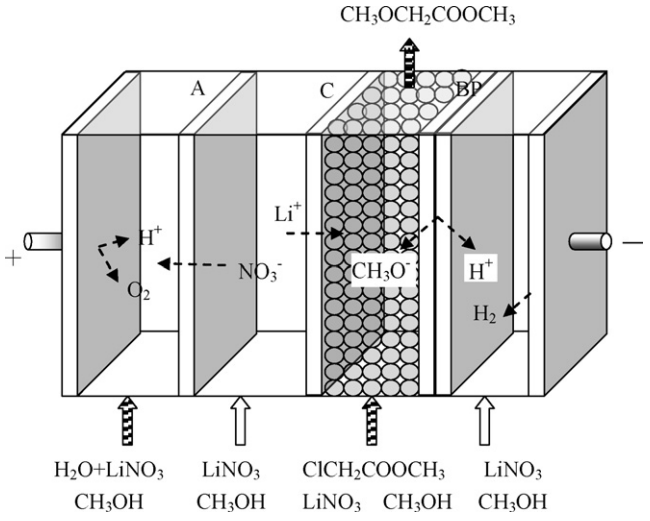

Fig. 1. Schematic of the experimental setup. A, anion-exchange membrane; C, cation-exchange membrane; BP, bipolar membrane.

2.3. Characterization of membranes and resins in methanol

2.3.1. Ion exchange capacity in methanol (IEC)

The cation-exchange membrane and cation-exchange resin were soaked in methanol solution of NaOH (0.01 mol L^{-1}, 20 mL) for 24 h, respectively. Then, the solution was titrated with a 0.01 mol L^{-1} HCl standard solution. The IEC value was calculated according to the following equation:

$$\mathrm{IEC}_+ = \frac{V_{\mathrm{NaOH}} \times C_{\mathrm{NaOH}} - V_{\mathrm{HCl}} \times C_{\mathrm{HCl}}}{w_{\mathrm{dry}}} \quad (2)$$

where w_{dry} is the dry weight of the sample in the Na^+ form; V_{NaoH} = 20 mL; C_{NaOH} = 0.01 mol L^{-1}; and C_{HCl} is the concentration of the HCl solution (0.01 mol L^{-1}); V_{HCl} is the titrated volume of the HCl solution.

For the anion-exchange membrane and anion-exchange resin, the IEC was measured the same as above. The IEC value was calculated according to the following equation:

$$\mathrm{IEC}_- = \frac{V_{\mathrm{HCl}} \times C_{\mathrm{HCl}} - V_{\mathrm{NaOH}} \times C_{\mathrm{NaOH}}}{w_{\mathrm{dry}}} \quad (3)$$

where w_{dry} is the dry weight of the sample in the Cl^- form; V_{HCl} = 20 mL; C_{HCl} = 0.01 mol L^{-1}; and C_{NaOH} is the concentration of the NaOH solution (0.01 mol L^{-1}); V_{NaOH} is the titrated volume of the HCl solution.

2.3.2. Methanol content and swelling ratio

The dried ion-exchange resins were weighed and immersed in methanol at 25 °C for 2 days, then filtrated under vacuum to remove methanol. The methanol content W was calculated according to the following equation:

$$W = \frac{w_{\mathrm{wet}} - w_{\mathrm{dry}}}{w_{\mathrm{dry}}} \times 100\% \quad (4)$$

where w_{wet} and w_{dry} are the wet and dry weights of the resins, respectively.

The swelling ration of ion-exchange membranes was characterized by linear expansion ration (LER) [13], which was determined by the difference between wet and dry dimensions of a membrane sample (3 cm in length and 1 cm in width). The calculation was based on the following equation:

$$\mathrm{LER} = \frac{L_{\mathrm{wet}} - L_{\mathrm{dry}}}{L_{\mathrm{dry}}} \times 100\% \quad (5)$$

where L_{wet} and L_{dry} are the lengths of wet and dry membranes, respectively.