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ORIGINAL PAPER

Electro-generation of 3-methyl-2-formylaminopyridine using a bipolar membrane as separator

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Abstract A mSA–mCS bipolar membrane was prepared by sodium alginate/polyvinyl alcohol (SA/PVA) and chitosan/polyvinyl alcohol (CS/PVA) modified by Fe^{3+} and glutaraldehyde as linking reagents, respectively. The mSA–mCS bipolar membrane was investigated by FT-IR, SEM, I–V curves, ion exchange capacity and changes of pH in the anode and cathode chambers. The SA–CS/PVA bipolar membrane was used as a separator in the electrolysis cell to electrogenerate 3-methyl-2-formylaminopyridine. The product yield was 49.8% and higher than that produced in a Nafion mono-membrane-equipped cell. Compared with the traditional chemistry method, the electro-generating process is moderate and eliminates pollution to the environment.

Keywords Bipolar membrane · Sodium alginate · Chitosan · Poly (vinyl alcohol) · 3-Methyl-2-formylaminopyridine

1 Introduction

The study of bipolar membranes (BPM) is important in the membrane field [1]. A BPM is a layered, polymeric structure composed of a cation ion exchange layer and an anion ion exchange layer. Protons and hydroxide ions are generated by splitting water at the interface with the help of an electrical field and these ions migrate to the cathode and anode, respectively. Due to its simplicity in usage, high efficiency, and low waste, BPM technology has already been applied in many industrial processes, especially in controlling pollution and regenerating acids and alkalis in the chemical industry [2–5]. For example, Xu et al. [6, 7] used macromolecules as the interfacial layer for catalyzing water dissociation. Yu et al. [8] reported the recovery of acetic acid from dilute wastewater using BPM. Bazinet et al. [9] developed an electro-acidification technology using BPM for the food industry. Sidhar [10] successfully synthesized acetoacetic ester using BPM with methanol splitting, which initiates novel and green paths for organic synthesis. Our laboratory has prepared thioglycolic acid [11] and FeO_4^{2-} [12], 2,2-dimethyl-3-hydroxyl propanoic acid using BPM as a separator [13].

The chemical 3-methyl-2-formylaminopyridine can be used to synthesize medicine to treat asthma, hypersensibility, HIV [14, 15] and sepsis [16]. It is also an enzyme catastaltic [17]. The traditional method for 3-methyl-2-formylaminopyridine production has many defects such as a low reaction rate and the difficulty of separating it from by-products. This study described the electro-generation of 3-methyl-2-formylaminopyridine by mSA–mCS BPM using 2-cyano-3-methylpyridine as the raw material, which was oxidized by MnO_2 in a dilute basic electrolyte solution. MnO_2 can be repeatedly generated in the anode chamber.

2 Materials and methods

2.1 Materials

Chitosan with an *N*-deacetylation degree of 90%, sodium alginate, PVA (molecular weight of 105,000 g mol^{-1}, 98.5 ± 0.5% hydrolyzed), glutaraldehyde (GA, 25% by

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weight in water), and iron trichloride were purchased from Guoyao Chemicals Co. Ltd. Poly (vinyl sulfate) potassium salt (PVSK), poly-diallyldimethylammonium chloride (PDADMAAC) and toluidine blue (TB) were purchased from Medicine and Chemicals Co., Japan. Methanol was of HPLC grade. The chemical 2-cyano-3-methylpyridine was purchased from Alfa Esar Co. Ltd. Other chemicals used were of analytical grade.

2.2 Preparations of mSA–mCS BPM

PVA solution was prepared by dissolving 3 g of PVA in 100 mL of distilled water with stirring for 1 h at 90 °C, and then kept at 25 °C for 24 h. The mixture of 60 mL sodium alginate (2 wt%) and 40 mL PVA solution was stirred for 2.5 h to make SA/PVA; this was then dried at room temperature. The SA/PVA membrane was cross-linked with 8% $FeCl_3$ aqueous solution for 1 h and dried to form a cation exchange layer at room temperature. This was denoted as mSA.

The mCS solution was made by mixing 60 mL chitosan (2 wt%) and 40 mL PVA (3 wt%) solution and stirring for 2.5 h with 0.25% glutaraldehyde as the cross-linking agent. Then, the mCS solution was poured on to the top of the mSA membrane and dried to form the anion exchange layer at room temperature.

2.3 Characterization of membrane

2.3.1 Swelling degree

Before the measurements, the membrane was immersed in 1 mol L^{-1} H_2SO_4 solution for 24 h at room temperature to reach the final dilation. Then, it was taken out of the solution and carefully wiped with absorbent paper before being weighed, W_s. W_d was obtained from the dried membrane at 80 °C in an oven. The degree of membrane swelling (S_w) was defined as:

$$S_w = (W_s - W_d)/W_d \times 100\%. \quad (1)$$

2.3.2 Co-ion leakage

Experiments on co-ion leakage through SA–CS/PVA BPM was carried out as described in the literature [9] using absorption spectrometry for Na^+ ions and chlorimetry for Cl^- ions:

$$t^{BPM} = \frac{C_t V_t - C_i V_i}{q_F} \quad (2)$$

$$r^{BPM}_{diss} = 1 - \left(t^{BPM}_{Na^+} + t^{BPM}_{Cl^-}\right) \quad (3)$$

where t^{BPM} is the number of chloride or sodium ions transported though the BPM; r^{BPM}_{diss} is the current efficiency of water dissociation; q_F is the amount of electrical charge carried by the current expressed in Faraday; C_iV_i and C_tV_t are the concentration and volume of sodium or chloride in the compartment at the initial time and at time t, respectively.

2.3.3 Exchange capacity

H^+ exchange capacity: Before the measurement, the membrane was immersed in 100 mL (0.1 mol L^{-1}) NaOH solution in a conical flask for 24 h at room temperature. The immerging solution (50 mL) was titrated by 0.1 mol L^{-1} HCl standard solution. The exchange capacity was calculated following Eq. 4:

$$IS_{H^+} = \frac{V_{NaOH} \cdot C_{NaOH} - V_{HCl} \cdot C_{HCl}}{W_{sample}(1 - \eta\%)} (\text{meq g}^{-1}). \quad (4)$$

OH^- exchange capacity: The membrane was washed with alcohol until the pour solution was neutral in tropeolin D. Then, the surface water was wiped with a filter paper and immediately weighed. The membranes were soaked in 500 mL (4%) Na_2SO_4. The soaking solution (50 mL) was titrated by 0.1 mol L^{-1} $AgNO_3$ using potassium chromate as indicator. The exchange capacity was calculated from Eq. 5:

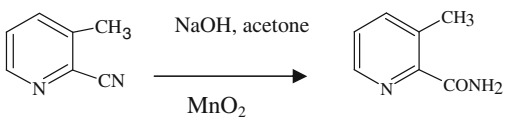
$$IS_{Cl^-} = \frac{V_{AgNO_3} \cdot C_{AgNO_3} \times 10}{W_{sample}(1 - \eta\%)} (\text{meq g}^{-1}) \quad (5)$$

where V: volume, mL; C: concentration, mol L^{-1}; W: mass, g.

The ionic exchange capacity for the cation layer (R-COONa)/anion layer (R-NH_3OH) in mSA–mCS BPM were 2.31 meq g^{-1} and 1.82 meq g^{-1}, respectively, similar to the value given in [18].

2.4 Mechanism of electro-generation of 3-methyl-2-formylaminopyridine

The synthetic reaction for preparing 3-methyl-2-formylaminopyridine is:



(6)

The raw material 2-cyano-3-methylpyridine used was oxidized by MnO_2 in a dilute basic electrolyte solution. MnO_2 can be repeatedly generated in the anode chamber. SA–CS/PVA BPM was used as a separator. The schematic of the mechanism for electrogenerated 3-methyl-2-formylaminopyridine is shown in Fig. 1.

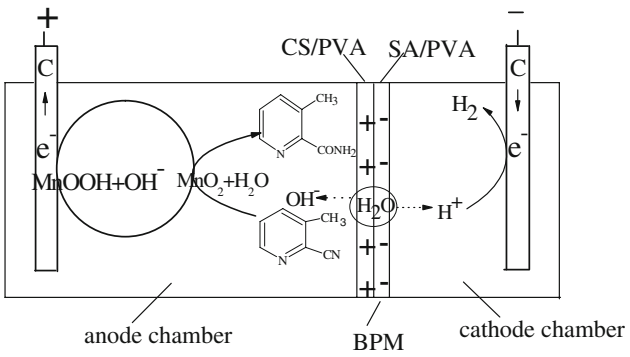


Fig. 1 Mechanism of electro-generated 3-methyl-2-formylaminopyridine using mSA–mCS BPM as the septum

A laboratory-scale electrolysis bath was composed of an anode chamber and a cathode chamber separated by mSA–mCS BPM. A graphite electrode (10 cm^2) was used as working electrode. The volumes of both the anode and cathode chambers were 110 mL. Na_2SO_4 (64 mL, 0.5 mol L^{-1}) was added to the cathode chamber as a supporting electrolyte. The starting materials (32 mL of 6% NaOH, 4.72 g of 2-cyano-3-methylpyridine, 3.48 g of MnO_2, and 32 mL of acetone) were added to the anode chamber. The reaction was kept in an ultrasonic atmosphere and the reaction temperature was 70 °C.

When the electrolysis began, MnOOH was oxidized to MnO_2, which served as an oxidant to convert 2-cyano-3-methylpyridine to 3-methyl-2-formylaminopyridine. Thus, an indirect electro-oxidation process was carried out in the cell. According to Eq. 6, the reaction should be kept in an alkali solution. In the BMP-equipped cell, OH^- was generated by splitting water at the BPM interface. These ions then migrated to the anode chamber to supply the OH^- for the electrochemical generation of 3-methyl-2-formylaminopyridine.

2.5 Measurement of 3-methyl-2-formylaminopyridine

A 5 U ODS3 liquid chromatographic column (LC-6A, Japan) was used to determine the concentration of 3-methyl-2-formylaminopyridine at room temperature. The mobile phase was comprised an aqueous solution of methanol and water; the volume ratio was 8:2 at a flow rate of 1 mL min^{-1}. The working wavelength of the UV detector was 265 nm.

3 Results and discussion

3.1 Scanning electron microscopy

The SEMs of the mSA–mCS membrane are shown in Fig. 2. As expected, a two-layer structure was observed (Fig. 2a). Both layers had a dense surface without pores. The upper layer (mCS) was close to a homogeneous surface (Fig. 2b), whereas the bottom layer (mSA) had a close-net structure (Fig. 2c). The distinct microcosmic phases of the two layers were attributed to the different composition and cross-linkage.

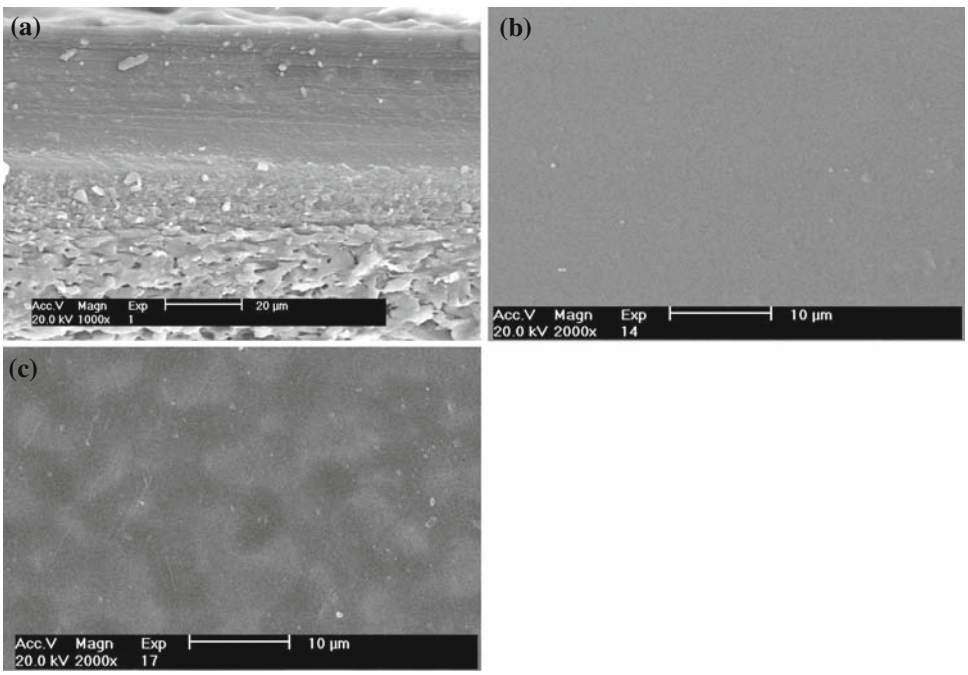


Fig. 2 SEM of mSA–mCS membrane. **a** Section view, **b** mCS layer, **c** mSA layer

3.2 FT-IR spectra

Figure 3 displays FT-IR spectra of PVA (a), CS (b), mCS (c), mSA (d), and SA (e) membranes. The FT-IR spectrum of pure PVA membrane showed absorption peaks at about 3296 cm^{-1} for the –OH group, at about 1419 cm^{-1} and 1091 cm^{-1} for the –C–O group. Figure 3c illustrates the effect of glutaraldehyde on the chemical structure of the mCS membrane. A broad absorption peak at the –OH group in PVA was found. The spectral change was due to the reaction between the hydroxyl groups and glutaraldehyde. Absorption of the $–NH_2$ group decreased because the reaction between glutaraldehyde and the $–NH_2$ group formed a –N=C bond [19]. A comparison between Fig. 3e and d membranes shows a weaker absorption peak of $–COO^-$ in mSA, suggesting that SA and PVA were modified by Fe^{3+} to form a cross-net structure. Hanada [20] suggests that pretreatment of the cation-exchange layer by heavy metal ions such as Fe^{2+}, Fe^{3+}, Ti^{4+}, Sn^{2+}, Sn^{4+}, Zr^{4+}, Pd^{2+}, and Ru^{3+}, will reduce the electrolysis voltage. This effect might be due to the special structure of the transition region. The heavy metal ions modified at the junction of BPM may result in a more hydrophilic phase that accelerates water dissociation [21].

The transport numbers of sodium and chloride through the BPM were 0.13 and 0.04, respectively and the current efficiency of water dissociation was 0.91 [22].

The IR spectra of chitosan (Fig. 3b) and glutaraldehyde-modified chitosan (Fig. 3c) (mCS) were investigated. The absorption of CS at 3000–3500 cm^{-1} was weaker. The hydrophilic property of the modified chitosan was obviously improved. The corresponding IR spectrum of mCS appeared as a broad absorption at 3000–3500 cm^{-1} (Fig. 3c).

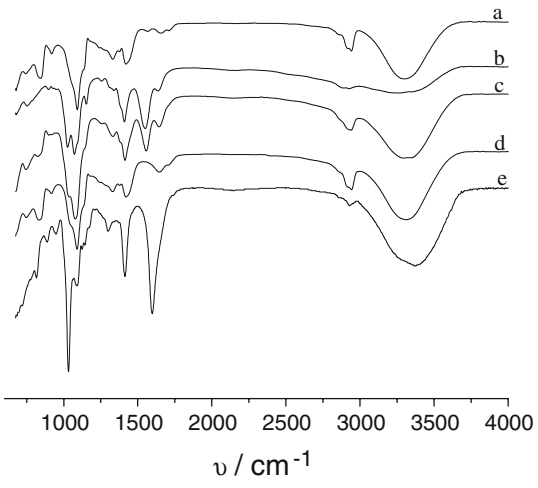


Fig. 3 Infrared spectra of PVA (**a**), CS (**b**), mCS (**c**), mSA (**d**), and SA (**e**) membranes

3.3 Water dissociation in the BPM junction region

Figure 4 plots the changes of pH in the anode and cathode chambers with time for 10 mA cm^{-2} in a neutral solution (0.5 mol L^{-1} of Na_2SO_4). For the Nafion mono-membrane, due to the evolution of oxygen at the anode, the anolyte turned acidic (Fig. 4). The reaction of oxygen evolution in the anode is shown in Eq. 7

$$2H_2O \rightarrow O_2 \uparrow + 4H^+ + 4e^-. \quad (7)$$

In contrast, due to the evolution of hydrogen, the catholyte appeared alkaline (Fig. 4). The cathode reaction is:

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^-. \quad (8)$$

Opposite results were observed in the mSA–mCS BPM-equipped cell (Fig. 4). The pH in the anode chamber increased with time but it decreased in the cathode chamber. This suggests that the protons and hydroxide ions generated by water splitting in the bipolar membrane moved to the cathode and anode chambers, respectively. This conclusion is consistent with the literature [23–26].

3.4 Measurement of I–V curves

As shown in Fig. 5, the electrolysis voltage increased as the current density went up. When the current density was below 50 mA cm^{-2}, both voltages of Nafion and BPM equipped cells went up slowly with increasing current density. When the current density was higher than 50 mA cm^{-2}, the voltage in the BPM-equipped cell rose sharply because of the formation of a depletion layer. The interface between the anode membrane and the cathode membrane is referred as a "space charge region" or "depletion layer" [27]. At higher current densities, water diffusion into the BPM interface should be slower than ion

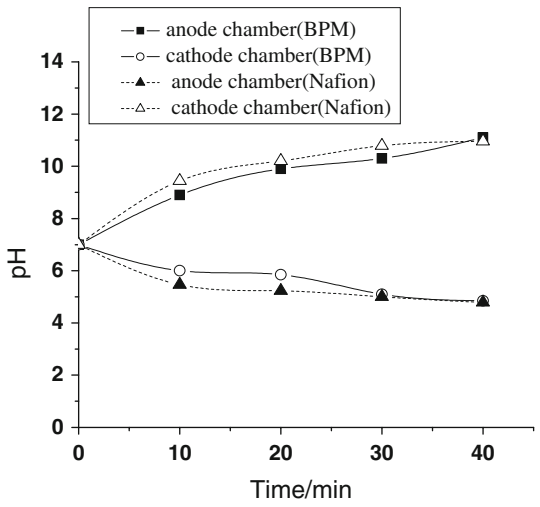


Fig. 4 Changes of pH in the anode and cathode chambers with time

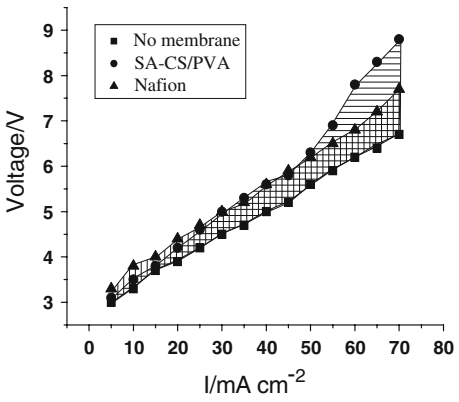


Fig. 5 I–V curves

electro-migration to the anode and cathode chambers. Thus, water dissociation would be hindered and the electrolysis voltage would rise sharply.

3.5 Product identification

The product was identified by IR and determination of the melting point. Figure 6 displays an IR spectrum of the product, 3-methyl-2-formylaminopyridin. Characteristic absorption peaks at 3420 cm^{-1} belong to the $–NH_2$ group, 3199 cm^{-1} to $–CH_3$ functional groups, 1688 cm^{-1} to the –C=O group, and 700–800 cm^{-1} to the pyridine group. The melting point, 140–141 °C measured by B tub is in agreement with the literature [28].

3.6 Electrogeneration of 3-methyl-2-formylaminopyridine

Using the Nafion mono-membrane or the mSA–mCS BPM as a septum to prepare 3-methyl-2-formylaminopyridine, the mole yields are shown in Fig. 7.

The product yield using the mSA–mCS BPM as a septum was higher than that using the Nafion mono-membrane as a septum. As shown in Eq. 6, the reaction for electrogeneration of 3-methyl-2-formylaminopyridine consumes OH^-. When Nafion was used as a septum, the product yield quickly decreased with the OH^- consumption in the anode chamber. In the case of BPM, because the hydroxide ions generated by water splitting at the interface of BPM move to the anode chamber to supply the hydroxide consumption, the product yield was maintained at 48% for a long time (2–4 h). Then the yield fell for reaction times beyond 4 h due to the reverse reaction, which caused 3-methyl-2-formylaminopyridine to be oxidized to carboxylic acid.

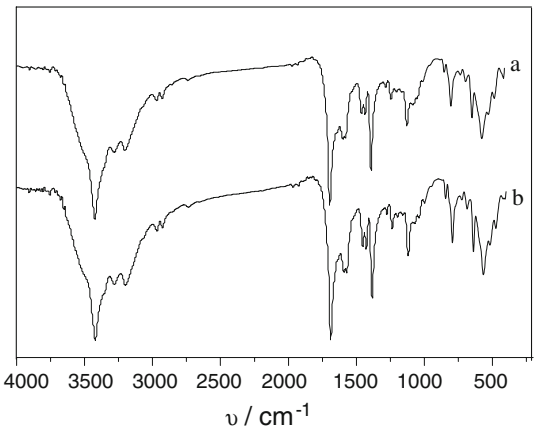


Fig. 6 Infrared spectra of 3-methyl-2-formylaminopyridine

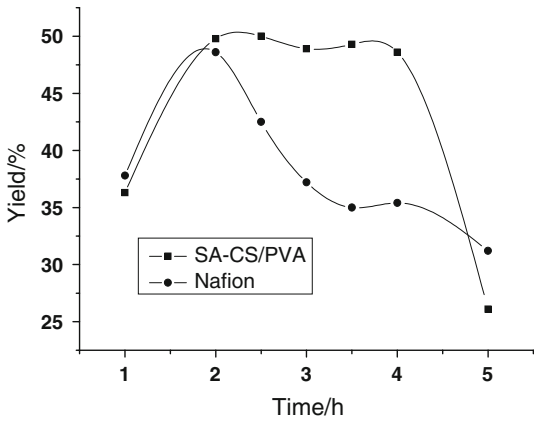


Fig. 7 The production rate with time

4 Conclusions

The natural low-cost sodium alginate/polyvinyl alcohol (mSA) and chitosan/polyvinyl alcohol (mCS) were modified by Fe^{3+} and glutaraldehyde as linking reagents, respectively. The mSA–mCS BPM was composed of a mSA cation layer and a mCS anion layer and was used as a separator in the electrolysis cell for electrogeneration of 3-methyl-2-formylaminopyridine. At the interface of the BPM, protons and hydroxide ions were generated by splitting water and migrated to the cathode and anode chamber, respectively. The OH^- consumption in the 3-methyl-2-formylaminopyridine producing reaction was effectively supplied. Compared with the traditional method, the electrogeneration process is benign and eliminates environmental pollution.

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