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Upgrading of Ethanol to 1,1-Diethoxyethane by Proton Exchange Membrane Electrolysis

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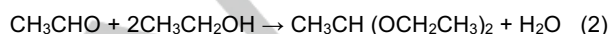
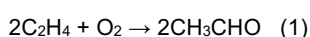
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Abstract: The direct acetalization of ethanol is a significant challenge for upgrading bioethanol to value-added chemicals. Herein, 1,1-diethoxyethane (DEE) was selectively synthesized by the electrolysis of ethanol using a proton exchange membrane (PEM) reactor. In the PEM reactor, a Pt/C catalyst promoted the electro-oxidation of ethanol to acetaldehyde. The Nafion membrane used as the PEM served as a solid acid catalyst for the acetalization of ethanol and electrochemically formed acetaldehyde. DEE was obtained at high Faradaic efficiency (78%) through sequential electrochemical and non-electrochemical reactions. The DEE formation rate through PEM electrolysis was higher than that of reported systems. At the cathode, protons extracted from ethanol were reduced to H₂. The electrochemical approach can be utilized as a sustainable process for upgrading bioethanol to chemicals because it can use renewable electricity and does not require chemical reagents (e.g., oxidants and electrolytes).

Introduction

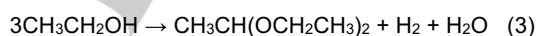
Currently, the chemical industry heavily relies on the use of petroleum. However, the depletion of fossil feedstock and the emission of carbon dioxide (CO₂) are pressing concerns. The use of biomass feedstock in the chemical industry is indispensable toward the realization of a sustainable future. Ethanol is expected to be a carbon-neutral raw material because ethanol is produced from biomass feedstock.^[1] Various value-added chemicals can be potentially synthesized from ethanol. Therefore, the direct conversion of ethanol to chemicals has been extensively investigated.^[2]

1,1-Diethoxyethane (DEE) is a derivative of ethanol and has versatile applications in the chemical industry. For example, DEE is an important intermediate in the production of chemicals such as alkyl vinyl ethers^[3] and a raw material in the fragrance industry.^[4] Furthermore, it serves as an efficient additive for diesel fuel or a biomass-derived solvent.^[5] At present, DEE is produced by a two-step process from ethylene and ethanol. The first step involves the synthesis of acetaldehyde by the oxidation of ethylene [Wacker process; Eq. (1)]. The second step includes the dehydrative condensation of acetaldehyde and ethanol in the presence of liquid acid catalysts [Eq. (2)].



This process inevitably has several drawbacks, namely, incompatibility with green chemistry principles because of the use of fossil resources (i.e., ethylene); toxicity and volatility induced by the formation of acetaldehyde; and corrosion of reactors using liquid acid.

To avoid these drawbacks, the direct synthesis of DEE from only ethanol is desired [Eq. (3)].



Several heterogeneous catalysts have been reported for this reaction.^[6] Among them, photo- and electrocatalytic systems are promising candidates because they can be utilized in the presence of solar power and renewable electricity, which are independent of fossil fuels. Although Pt/TiO₂ and CdS/Ni-MoS₂ were found to be effective for the photocatalytic synthesis of DEE,^[7] the electrochemical synthesis of DEE has rarely been reported. McElwee-White et al. reported the electro-oxidation of ethanol to DEE using homogeneous catalysts (i.e., carbonyl-containing Ru and Fe heterobimetallic complexes).^[8] However, DEE showed a low (<30%) Faradaic efficiency (FE), and the indispensable separation of both electrolytes (alkylammonium salt) and homogeneous catalysts from the products was difficult. Recently, our research group reported the dehydrogenative conversion of methanol to methyl formate through proton exchange membrane (PEM) electrolysis.^[9] Compared to conventional electrolysis systems, PEM electrolysis has the following advantages:^[10] (i) the separation of products is easier because electrolytes are not present in the solution (as the PEM serves as a solid-state electrolyte), and (ii) the iR drop can be minimized because of the proximity of the cathode and anode, resulting in high energy-conversion efficiency.

Although the electrolysis process for upgrading ethanol to valuable chemicals such as acetic acid and ethyl acetate has been reported,^[11] DEE synthesis from ethanol through PEM electrolysis has not been investigated. This is the first study to report selective DEE synthesis from ethanol through PEM electrolysis (Figure 1). The sequential processes of electrochemical and non-electrochemical reactions are key to DEE production. The water content in ethanol controls the FE of

DEE synthesis. Moreover, we found that PEM acts not only as a proton conductor but also as a solid acid catalyst for acetalization. The reaction mechanism for DEE synthesis through PEM electrolysis is discussed in detail.

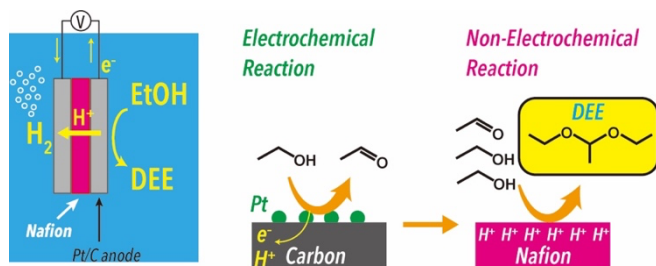


Figure 1. Schematic diagram for the PEM electrolysis of ethanol.

Results and Discussion

Effect of water on electrolysis of ethanol

To date, the electrochemical conversion of ethanol has been typically conducted in the presence of water. In this study, we found that the coexistence of water negatively affected the electrosynthesis of DEE from ethanol. Figure 2a shows the FE for the anode products obtained from the electrolysis of 100% ethanol and aqueous ethanol solution (volume fraction of water to ethanol = 0.33 and 0.67). Evidently, the electrolysis products of ethanol were significantly affected by the water content. The electrolysis of aqueous ethanol solution mainly produced acetaldehyde, and the amount of FE for acetaldehyde increased with the water content. In contrast, the electrolysis of 100% ethanol afforded DEE dominantly (FE \approx 70%), and a trace amount of acetaldehyde was produced. Gas chromatography/mass spectrometry (GC-MS) revealed the formation of DEE (Figure S1). In addition, small amounts of acetic acid and ethyl acetate were formed. Results shown in Figure 2 suggest that the coexistence of water in ethanol negatively affected the FE of the synthesis of DEE, and DEE was formed at high FE (\sim 70%) from the electrolysis of 100% ethanol. It should be noted that this is the first report on the selective synthesis of DEE by PEM electrolysis of ethanol.

In this study, gas chromatography (GC) was conducted to quantitatively analyze the possible products (i.e., acetaldehyde, DEE, acetic acid, ethyl acetate, and CO₂), but the total FE of the reactions forming these products was <100%. We consider that the Nafion membrane absorbed some of the products. The Nafion membrane swelled after electrolysis, indicating that it could absorb organic molecules. The electrolysis products are formed near the Nafion membrane; therefore, some of the products might be absorbed in the Nafion membrane, and the total FE would not reach 100%. Indeed, we tested the absorption of an anode product in the Nafion membrane. Immersing the Nafion membrane into a solution containing acetaldehyde for 1 h, we found that the amount of acetaldehyde decreased by 19%, indicating acetaldehyde was absorbed in the Nafion membrane.

In the electrolysis shown in Figure 2, the oxygen evolution reaction (OER) by water electrolysis hardly occurs. As mentioned in the experimental section, the potential at the

cathode can be regarded as a quasi-reference electrode (a standard hydrogen electrode: SHE), and the electrolysis voltage was 1.2 V, indicating that the potential at the anode was approximately 1.2 V vs. SHE. The standard redox potential for the OER is +1.23 V vs. SHE; therefore, the OER rarely occurs in the electrolysis at 1.2 V. Furthermore, we performed electrolysis of ethanol and aqueous ethanol solutions at 1.0 V (Figure S2). OER cannot occur at 1.0 V of electrolysis. In this case, the total FE was also less than 100%, indicating the loss of FE was not attributed to OER.

Figure 2b shows time course of PEM electrolysis of ethanol solution with different water contents as a function of current density. For all cases, high current density flowed at the initial stage of electrolysis, and a constant current of 20–30 mA cm⁻² was observed. The presence of water slightly increases the current density.

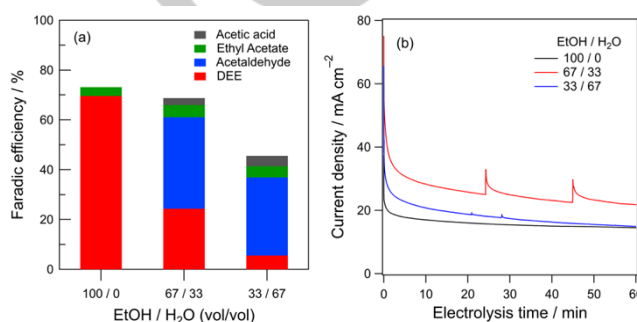


Figure 2. (a) FE of product formation at the anode and (b) time course of the electrolysis of an ethanol solution and ethanol solutions with different water contents at 1.2 V as a function of current density.

Figure 3 shows the linear sweep voltammetry (LSV) curves for ethanol and aqueous ethanol solutions using the PEM reactor. The onset voltage for ethanol oxidation was 0.5 V, and the anodic current increased with electrolysis voltage. The same onset voltage for all solutions implies that the same electrochemical reaction proceeds at 0.5 V. The two-electron oxidation of ethanol to acetaldehyde considerably progressed. Furthermore, similar to the electrolysis results, the current density increased with the water content. The trend of increasing current density in the presence of water may be assumed to be due to the water-induced transportation of protons in Nafion, which is typically observed in fuel cell systems.^[12]

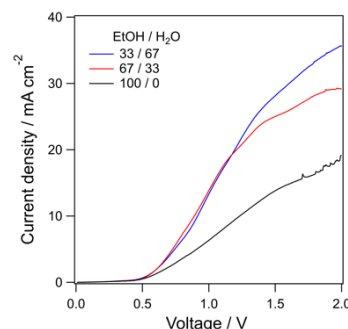
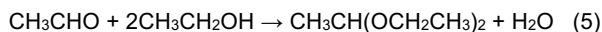
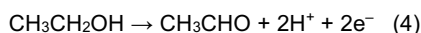


Figure 3. LSV curves for an ethanol solution and aqueous ethanol solutions with different water contents using the PEM reactor.

Nafion as a solid acid catalyst for acetalization

In the PEM electrolysis, we considered that the following successive reactions formed DEE:



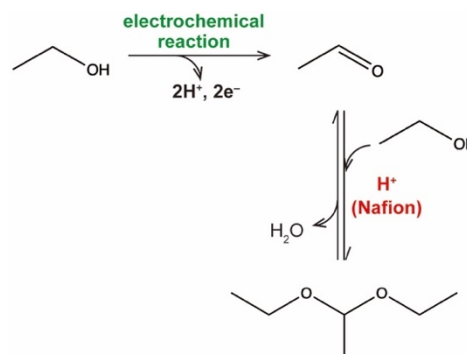
The electrolysis of ethanol provided acetaldehyde [Eq. (4)], and then the non-electrochemical reaction of acetaldehyde and ethanol forms DEE [Eq. (5)]. Acetaldehyde is a typical product of the ethanol electro-oxidation over Pt catalysts.^[13] In this study, acetaldehyde was the dominant product in the electrolysis of aqueous ethanol solution (Figure 2a). Furthermore, acetaldehyde was formed at 95% of FE by electrolysis of ethanol on Pt without using MEA. Therefore, it is likely that the PEM electrolysis of ethanol over the Pt/C catalysts formed acetaldehyde.

The dehydrative condensation of aldehyde and alcohol to form DEE [Eq. (5)] is the next step. In general, acetalization requires acid catalysts, but acid electrolytes, such as H_2SO_4 , are not used in this study. Capeletti et al. reported that the use of a sulfonic ion-exchange resin promoted the formation of DEE from ethanol and acetaldehyde.^[14] Hence, we focused on the Nafion membrane that serves as a proton conductor in the PEM reactor. Because Nafion can act as a solid acid owing to the presence of a sulfonic acid group,^[15] the acid catalysis of Nafion could promote acetalization. To clarify the role of the Nafion membrane in DEE synthesis, we performed acetalization under non-electrochemical conditions in the absence or presence of Nafion. Table 1 summarizes the results. The DEE yield was significantly affected by the presence of Nafion. In the absence of Nafion (entry 1), no DEE was formed, whereas a high DEE yield (81%) was achieved in the presence of Nafion (entry 2), indicating that Nafion catalyzed the acetalization of ethanol and acetaldehyde. The results suggested that the Nafion membrane acted as a solid acid catalyst, and the electrochemically formed acetaldehyde was converted to DEE.

Table 1. Acetalization of acetaldehyde and ethanol under non-electrochemical conditions.

Entry	Volume / mL			Nafion	DEE yield / %
	Ethanol	Acetaldehyde / N, N-dimethylformamide	Water		
1	30	1	0	absent	0
2	30	1	0	present	80.7
3	20	1	10	present	22.2
4	10	1	20	present	10.8
5	0	1	30	present	0

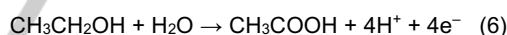
Based on the above results, we propose the synthetic route for DEE by PEM electrolysis, as shown in Scheme 1. First, the two-electron oxidation of ethanol provides acetaldehyde, which is a widely accepted route for the electro-oxidation of ethanol over Pt catalysts. The dehydrative condensation of acetaldehyde and ethanol yields DEE, wherein Nafion acts as a solid acid catalyst.



Scheme 1. Proposed mechanism for selective DEE synthesis from ethanol through PEM electrolysis.

Dehydrative acetalization is a reversible reaction; therefore, water is unfavorable for DEE formation. As shown in Table 1 (entries 2–4), acetalization under non-electrochemical conditions was suppressed when the water content increased. Therefore, the water content changed the ethanol electrolysis products. As shown in Figure 2a, FE for DEE was high for the electrolysis of 100% ethanol, while FE for DEE decreased and FE for acetaldehyde increased with increasing water content. Scheme 1 shows that acetaldehyde and DEE form successively; therefore, the presence of water reverses acetalization, and acetaldehyde is mainly produced by suppressing the formation of DEE. Furthermore, the anode products (acetaldehyde and DEE) were hardly oxidized in the anodic region (Figure S3), indicating that they are not decomposed at the anode.

Ethyl acetate and acetic acid were the minor products in this study. Acetic acid was detected in the electrolysis of aqueous ethanol solution (FE = 2.8–4.2%), but not of 100% ethanol, because both water and ethanol are necessary to form acetic acid [Eq. 6].



The electrolysis of ethanol and aqueous ethanol solution produced a small amount of ethyl acetate (FE = 3.6%–4.9%). Ethyl acetate is produced by the dehydrative condensation of ethanol and acetic acid (i.e., Fischer esterification). However, in PEM electrolysis, ethyl acetate is formed via a different pathway. In our study, ethyl acetate was detected in 100% ethanol electrolysis, wherein acetic acid could not be formed. Therefore, the following reaction might form ethyl acetate.^[16]



It has been reported that CO_2 can be formed by the electro-oxidation of an aqueous ethanol solution. To analyze CO_2 , an ethanol solution or an aqueous ethanol solution (ethanol/water = 33/67, vol/vol) was bubbled with He, and the outlet gas during electrolysis at 1.2 V was analyzed by GC. However, in the both case, CO_2 was not produced through the proposed reaction system; thus, it was not detected. Furthermore, although a trace amount of ethane was detected in the GC analysis, the effect of ethane on FE was negligible.

Electrolysis of pure ethanol

The effect of the applied voltage on the electrolysis of 100% ethanol was examined (Figure 4). Regardless of the electrolysis voltage, DEE was dominantly formed, and FEs for DEE were 70%–78% (Figure 4a). The time courses of the electrolysis as a function of current density were similar at all electrolysis voltages (Figure 4b); a high current was detected at the initial stage of electrolysis, followed by a constant current. The oscillation of current density was observed for the electrolysis at 1.6 and 2.0 V. This was previously observed in the electrochemical measurements for ethanol oxidation and can be attributed to the presence of species containing C=O groups (acetaldehyde and acetic acid).^[17]

The electrolysis productivity can be evaluated by the current density and FE. In this study, the current density increased with electrolysis voltage (Figures 3 and 4b), while FE for DEE was stable at all voltages; therefore, a high formation rate of DEE was achieved at high voltage. The highest DEE formation rate (670 mmol g_{cat}⁻¹ h⁻¹) was observed at 2.0 V (Figure 4a). Evaluating the number of surface Pt atoms from the cyclic voltammogram of Pt/C (Figure S4), we estimated the turnover frequency (TOF) of the electrolysis system to be 1858 h⁻¹.

The DEE formation rates achieved in this study and those reported in previous works are listed in Table S1. The DEE formation rate achieved by our system (670 mmol g_{cat}⁻¹ h⁻¹) is higher than those of the flow systems using heterogeneous catalysts (5–12 mmol g_{cat}⁻¹ h⁻¹),^[6b-d] photocatalytic systems (8–158 mmol g_{cat}⁻¹ h⁻¹),^[7a-d] and liquid phase reactions with homogeneous catalysts (40 mmol g_{cat}⁻¹ h⁻¹).^[18] The high formation rate suggested that the electrocatalytic approach is potentially practical to synthesize DEE.

To verify the stability of the electrolysis system, ethanol was electrolyzed at 2.0 V for 12 h. The results are presented in Figure 5. A stable current density was observed for 12 h, indicating that the deactivation or dissolution of the electrocatalysts did not occur and that the degradation of the PEM reactor did not occur. DEE was the main product after 12 h of electrolysis, and high FE for DEE was maintained (72%).

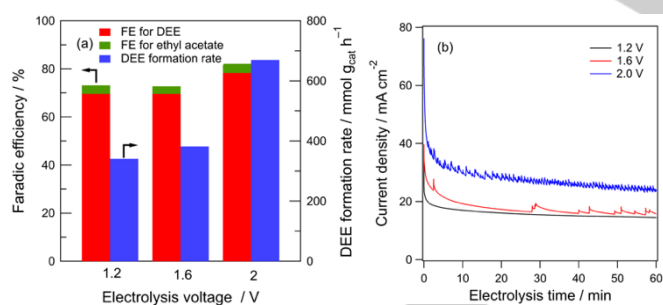


Figure 4. (a) FE of anode products and (b) time course of the electrolysis of 100% ethanol with different electrolysis voltages as a function of current density.

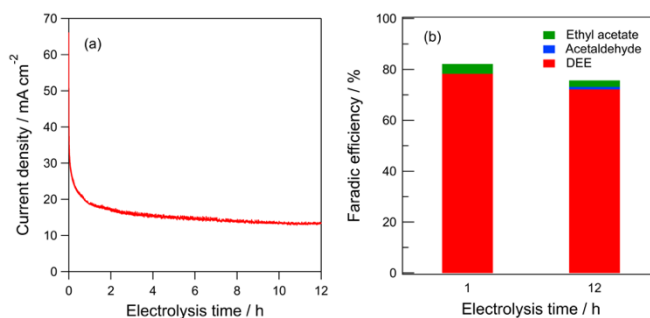
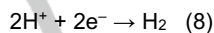


Figure 5. (a) Time course of the electrolysis as a function of current density and (b) FE of anode products for electrolysis of 100% ethanol at 2.0 V for 12 h.

Hydrogen production on cathode

Finally, we discuss the formation of H₂ at the cathode. In PEM electrolysis, as shown in Figure 1, protons are extracted from ethanol on the anode and transported toward the cathode through the Nafion membrane. Subsequently, the proton is electrochemically reduced to H₂ gas [Eq. (8)].



In the PEM reactor, gas diffusion layers (GDLs) deposited with Pt/C catalysts were used as the cathode and anode. Pt/C promoted acetaldehyde formation on the anode and H₂ production on the cathode. H₂ formed on Pt/C diffuses the GDLs and is released into the liquid phase. The structure of the PEM reactor was examined using cross-sectional field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray (EDX) mapping images (Figure 6). From the FE-SEM image, it is observed that the GDL contacted the Nafion membrane. The EDX mapping images indicated that Pt was present at the interface between the GDL and Nafion membrane. Figure 7 shows almost 100% FE for H₂ during electrolysis, which supports the production of only H₂ at the cathode.

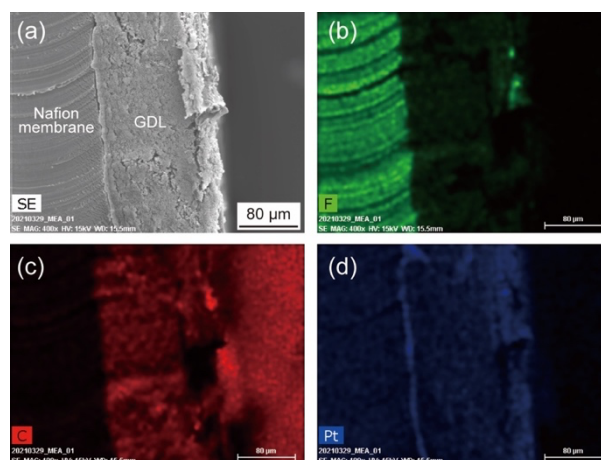


Figure 6. (a) FE-SEM and EDX mapping images for (b) F, (c) C, and (d) Pt from a cross-section of the PEM reactor.

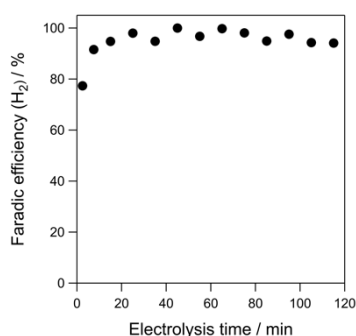


Figure 7. Time course of the electrolysis of ethanol at 2 V as a function of FE for H₂.

It should be emphasized that one of the advantages of the DEE synthesis by PEM electrolysis is the co-production of H₂. H₂ is an essential feedstock for the current chemical industry and is expected to be a future energy source in fuel cells.^[19] In this regard, the electrolysis of organic molecules to form both value-added chemicals and H₂ has been intensively studied.^[20] The proposed approach leads to the formation of not only value-added chemicals (DEE) but also H₂, making it a valuable strategy. Furthermore, the PEM electrolysis of ethanol requires no chemical reagents (e.g., oxidants and electrolytes) and can be conducted by using renewable electricity. These are desirable features from the viewpoint of green synthesis for chemicals and the realization of a sustainable future.

Conclusion

The PEM electrolysis of ethanol selectively produced DEE. In the electrolysis of pure ethanol, DEE was formed at high FE (78%). DEE formation proceeded via sequential electrochemical and non-electrochemical reactions. First, ethanol was electrochemically oxidized to acetaldehyde over Pt/C. The second step involved the acetalization reaction. Because the Nafion membrane in the PEM reactor served as a solid acid catalyst, acetaldehyde reacted with ethanol to form DEE. The formation rate of DEE by PEM electrolysis at 2 V was 670 mmol g_{cat}⁻¹ h⁻¹, which is higher than that of other systems. An advantage of DEE synthesis by PEM electrolysis is the co-production of H₂ on the cathode, indicating that the PEM electrolysis of ethanol provides value-added products on both the anode (DEE) and cathode (H₂). The formation of DEE was suppressed by increasing the water content in ethanol because dehydrative acetalization is a reversible reaction. In PEM electrolysis, renewable electricity can be used and chemical reagents (e.g., oxidants and electrolytes) are not required. These factors enable the implementation of the electrochemical approach as a sustainable process for upgrading bioethanol to value-added chemicals.

Experimental Section

Materials

Ethanol (Kanto Chemical Co., Inc.), acetaldehyde (~2% in N, N-dimethylformamide; Tokyo Chemical Industry Co., Ltd.), DEE (Tokyo Chemical Industry Co., Ltd.), N, N-dimethylformamide (Kanto Chemical Co., Inc.), ethyl acetate (Kanto Chemical Co., Inc.), butyl acetate (Wako Pure Chemical Corp.), acetonitrile (FUJIFILM Wako Pure Chemical Corp.), 30% hydrogen peroxide (Kanto Chemical Co., Inc.), 10 wt% Nafion™ dispersion solution (DE1021 CS type; Wako Pure Chemical Corp.), 1 M H₂SO₄ (Kanto Chemical Co., Inc.), 0.5 M H₂SO₄ (FUJIFILM Wako Pure Chemical Corp.), and tetrabutylammonium tetrafluoroborate (Tokyo Chemical Industry Co., Ltd.) were used as received. Pt/C (50 wt%; TEC10E50E) was purchased from Tanaka Kikinzoku Kogyo K.K. (TKK). Nafion perfluorinated membranes (Nafion 117) were purchased from Techno Sigma Co., Ltd. These membranes (2 cm × 2 cm) were pretreated with (1) 3% aqueous H₂O₂ solution, (2) deionized water, (3) 1 M H₂SO₄, and (4) deionized water on a hot plate at 140 °C for 1 h.

Preparation of membrane electrode assembly (MEA)

The MEA used in this study was prepared in the same way as that reported in our previous work.^[9] The catalyst ink was prepared by the sonication of 50 wt% Pt/C (2 mg), ethanol (1 mL), and 10 wt% Nafion perfluorinated resin solution (25 μL). An equal amount of ink was dropped onto two GDLs (SIGRACET 29BC) with a circular area of 1.65 cm² on a hot plate at 413 K (0.6 mg_{cat} cm⁻²_{GDL}). After drying the GDLs at 403 K for 10 min, they were used as the cathode and anode. Next, a Nafion membrane (2 × 2 cm²) was pressed between the cathode and anode at 413 K under 20 MPa for 10 min. The obtained unit was used as the MEA.

PEM electrolysis of ethanol

The PEM reactor was composed of the MEA and current collectors, as described in our previous work.^[9] Figure 1 shows a schematic image of the PEM reactor. The PEM reactor was immersed in a 100% ethanol solution or aqueous ethanol solution (volume fraction of H₂O = 0.67 or 0.33). Next, by stirring the solution and flowing He (10 mL min⁻¹), the electrolysis of ethanol was carried out at a constant voltage (1.2, 1.6, and 2.0 V) for 1 or 12 h by using a potentio/galvanostat (HA-151A, Hokuto Denko Co.). The current and voltage during electrolysis were recorded using a data logger (GL240, Graphtec Co.).

The electrolysis products were analyzed using GC. Acetaldehyde in the gas phase was analyzed using GC-8A (TCD, Shimadzu Corp.) with a Porapak R column under flowing He as the carrier gas. The gas-phase products were analyzed every 10 min. After electrolysis, the solution was cooled in an ice bath to prevent the vaporization of the products. The solution was then injected into GC-8A to analyze acetaldehyde. The other products in the liquid phase (DEE, ethyl acetate, and acetic acid) were analyzed using GC-18A (FID, Shimadzu Corp.) with DB-624UI (Agilent Technologies, Inc.) under flowing N₂ as the carrier gas. In the analysis with GC-18A, butyl acetate was used as an internal standard. As shown in Figure 1, the cathode and anode compartments were not separated. Thus, gas-phase and liquid-phase contained the products from both anode and cathode.

FE was calculated on the basis of the charge to synthesize the anode products (DEE, acetaldehyde, acetic acid, and ethyl acetate) and the total charge passed during electrolysis [Eq. (9)].

$$\text{FE (\%)} = (\text{charge to form products}) / (\text{total charge passed}) \times 100 \quad (9)$$

To determine the FE of H₂ production, we performed the electrolysis of a pure ethanol solution at 2 V under flowing Ar (10 mL min⁻¹) for 2 h. During the electrolysis, H₂ in the outlet gas was analyzed using GC-8A (TCD, Shimadzu Corp.) with an active carbon column under flowing Ar as the carrier gas.

Electrochemical measurement

LSV of ethanol or aqueous ethanol solutions (volume fraction of H₂O = 0.67 or 0.33) was conducted using the PEM reactor. The anode and cathode were the working and counter electrodes, respectively. On the cathode, the hydrogen evolution reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) proceeded; therefore, the potential at the cathode can be regarded as a quasi-reference electrode, i.e., as SHE. LSV was carried out using a potentiostat/galvanostat (HA-151A, Hokuto Denko Co.) with a function generator (HB-305, Hokuto Denko Co.) and the output was recorded using a data logger (GL240, Graphtec Co.) at a scan rate of 1 mV s⁻¹; the 1st cycle of LSV was recorded.

Electrolysis of ethanol without MEA

Electrolysis of ethanol without MEA was carried out using three-electrode system. Pt black deposited on Pt wire was used as working and counter electrodes. Ag/AgCl was used as a reference electrode. Ethanol containing 0.1 M tetrabutylammonium tetrafluoroborate was electrolyzed at 2.0 V vs Ag/AgCl under vigorous stirring for 3 h. The electrolysis solution was analyzed with GC.

Acetalization of acetaldehyde and ethanol under non-electrochemical conditions

The following mixture solution was prepared.

- Ethanol (30 mL) and ~2% acetaldehyde in N, N-dimethylformamide (1 mL)
- Ethanol (20 mL), water (10 mL), and ~2% acetaldehyde in N, N-dimethylformamide (1 mL)
- Ethanol (10 mL), water (20 mL), and ~2% acetaldehyde in N, N-dimethylformamide (1 mL)
- Water (30 mL) and ~2% acetaldehyde in N, N-dimethylformamide (1 mL)

The solution was magnetically stirred for 1 h at room temperature with or without the Nafion membrane (2 × 2 cm²). The Nafion membranes were dried at 403 K for 10 min before immersion in the solution. DEE was analyzed using GC-18A (FID, Shimadzu Corp.) with DB-624UI (Agilent Technologies, Inc.) under flowing N₂ as the carrier gas. The DEE yield was calculated as follows [Eq. (10)]:

DEE yield (%) = amount of formed DEE (mol) / amount of acetaldehyde

in the reaction solution (mol) × 100 (10)

Absorption of products in Nafion membrane

30 mL of acetonitrile/water solution was prepared (acetonitrile/water = 67/33, vol/vol), and then 1.0 mL of 2% acetaldehyde in N, N-dimethylformamide was added. A dried Nafion membrane (2 × 2 cm²) was immersed into the solution and kept at room temperature for 1 h. The amount of acetaldehyde in the solution was analyzed with GC.

Characterization

FE-SEM was conducted on the S-4800 system (Hitachi High-Technologies) at an acceleration voltage of 15 kV. EDX analysis was performed using a Quantax 400 device with an XFlash 4010 system (Bruker) equipped with the S-4800 apparatus. The cross-sectional specimen was prepared by cutting the MEA with a razor (Nissshin EM Co., Ltd.). The identification of DEE was performed through GC/MS (Bruker, SCION SQ), wherein the system was equipped with a capillary column (Bruker, BR-5 ms, 0.25 mm i.d., 30 m).

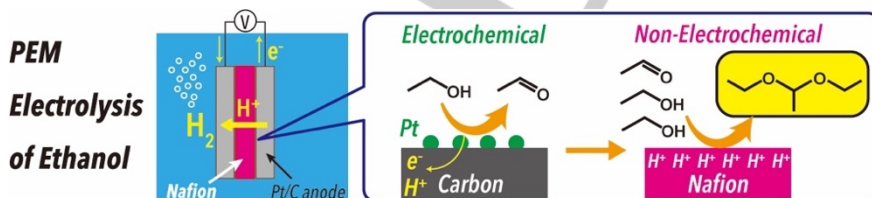
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Keywords: 1,1-diethoxyethane • ethanol • proton exchange membrane (PEM) reactor • electrolysis • catalysis

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1,1-diethoxyethane was selectively synthesized by the electrolysis of ethanol using a proton exchange membrane (PEM) reactor. In the PEM reactor, a Pt/C promoted the electro-oxidation of ethanol to acetaldehyde. The Nafion membrane used as the PEM served as a solid acid catalyst for the acetalization of ethanol and acetaldehyde. The proposed electrochemical approach can be utilized as a sustainable process for upgrading bioethanol to chemicals. (448 characters)