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Novel Composite Electrolyte Membranes Consisting of Fluorohydrogenate Ionic Liquid and Polymers for the Unhumidified Intermediate Temperature Fuel Cell

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Abstract

Novel composite electrolyte membranes consisting of [EMIm](FH)_nF (EMIm = 1-ethyl-3-methylimidazolium, $n = 1.3$ and 2.3) ionic liquids and fluorinated polymers were synthesized and their physical and electrochemical properties were measured under unhumidified conditions for their application to the intermediate temperature fuel cells. The ionic conductivities of composite membrane, P(VdF-co-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75 in weight ratio), were 11.3 and 34.7 mS cm⁻¹ at 25 and 130°C, respectively. The open circuit voltage (OCV) observed for the single cell using [EMIm](FH)_{2.3}F composite electrolyte was ~1.0 V at 130°C for over 5 h. The maximum power density of 20.2 mW cm⁻² was observed under the current of 60.1 mA cm⁻² at 120°C. From the high thermal stability and high ionic conductivity, the fluorohydrogenate ionic liquid composite membranes are regarded as promising candidates for the electrolytes of the unhumidified intermediate temperature fuel cells.

Keywords: Ionic liquid; Fluorohydrogenate; Polymer; Composite electrolyte membrane; Ionic conductivity; Fuel cell

1. Introduction

Recently, many researches have concentrated on the polymer electrolyte fuel cells (PEFCs) for a wide variety of their promising applications such as stationary power supply, electric vehicle, power sources in space and military [1-5]. The commercialization of PEFCs, however, is being hampered by several serious obstacles such as the difficulty of water and temperature control, necessity of a large amount of expensive Pt catalyst, and its poisoning by carbon monoxide (CO).

Nafion[®] ionomer membranes have been most widely studied and used in PEFCs because of their excellent chemical, physical, and electrical properties [6,7]. The major drawback of the Nafion[®] membranes, however, is that the conductivity drops at temperatures higher than 100°C due to the evaporation of water. High cost due to the complex synthetic process and the low thermal stability at high temperatures are also disadvantages of Nafion[®] for PEFC applications.

Most of these problems might be solved if PEFC could be operated at higher temperature than 100°C without humidification [3-5,8-11]. Firstly, CO is competitively adsorbed on the Pt anode electrocatalyst with H₂. The absolute free energy of adsorption of CO on Pt decreases more rapidly with the temperature elevation than that of H₂. The CO tolerance of Pt, therefore, is improved at elevated temperatures over 100°C. Secondly, higher temperature operation can simplify the thermal management. A smaller cooling system is desirable and the generated heat can be used effectively. Also, it increases

reaction rates at both electrodes to improve the power generation efficiency and decrease the amount of Pt catalyst. Finally, the problem of water management also can be solved very easily. The unhumidified PEFC do not use water, therefore, it can be operated at over 100°C without deterioration of the cell performance without water management.

Recently, several proton conducting membranes were developed for high temperature operation, including modified perfluorosulfonic acid (PFSA) polymer membranes, alternative sulfonated polymers and their inorganic composite membranes, acid-base complex membranes, and ionic liquid-based gel-type proton conducting membranes [3,5,12-23].

From a sheer independent standpoint, we have proposed and reported that a fuel cell operable without humidification can be constructed using a room temperature ionic liquids (RTILs), 1-ethyl-3-methylimidazolium fluorohydrogenates, [EMIm](FH)_nF (*n* = 1.3 and 2.3) [24]. Since hydrogen is transported via fluorohydrogenate anions, (FH)_nF⁻, in this fuel cell, we named it fluorohydrogenate fuel cell (FHFC). In the present paper, we prepared novel composite electrolyte membranes consisting of [EMIm](FH)_nF and polymeric matrix containing sulfonate group to immobilize ILs, and measured their physical and electrochemical properties. The fuel cell performance was also investigated using these composite membranes at temperatures over 100°C without humidification.

2. Experimental

[EMIm](FH)_nF ($n = 1.3$ and 2.3) were prepared according to the previous report [25]. Poly(vinylidene fluoride-*co*-hexafluoropropylene) (P(VdF-*co*-HFP), Aldrich) and other reagents were used as received. The sulfonated-fluorinated poly(arylene ether) was prepared from decafluorobiphenyl (DFBP, Wako) and 4,4'-(hexafluoropropylidene)diphenol (HFDP, Aldrich) by the modified synthetic methods reported previously [26].

2.1. The preparation of the poly(decafluorobiphenyl-(hexafluoropropylidene)diphenol (DFBP-HFDP))

A mixture of 3.40 g (10 mmol) of decafluorobiphenyl, 3.43 g (10 mmol) of 4,4'-(hexafluoropropylidene)diphenol, and 70 mL of *N,N*-dimethylacetamide were put in a 250 mL round bottomed flask equipped with a condenser and stirred until the mixture was completely dissolved. Potassium carbonate (Wako, 4.14 g, 30 mmol) was added to the mixture and heated up to 160°C. After 2 h of heating and stirring, the reaction mixture was poured into rapidly stirred distilled water containing 1 wt.% of acetic acid to precipitate the polymer. The precipitates were filtered and washed with distilled water until the pH reached neutral to remove the excess potassium carbonate and acetic acid. A white powdery DFBP-HFDP was obtained after drying.

2.2. Sulfonation and casting

The general procedure of sulfonation is as follows: DFBP-HFDP (2.0 g) was dissolved in 100 mL of chloroform in a flask equipped with a condenser. Then, 20 times mole of fuming sulfuric acid (30% SO₃) to DFBP-HFDP was added into the flask dropwise and the mixture was vigorously stirred at room temperature for 4 h. The sulfonated DFBP-HFDP (s-DFBP-HFDP) was precipitated in distilled water and then filtered. To remove unreacted sulfuric acid, the s-DFBP-HFDP was washed with distilled water until the pH of the washed water reached neutral. A pale brown powdery s-DFBP-HFDP was obtained after drying. Composite membranes were prepared by casting method by pouring the solution mixture of polymers and ionic liquids in a Teflon dish to evaporate solvent. The thickness and size of the membranes were varied by controlling the volume of the solution and the diameter of the plates.

2.3. Characterizations

A differential scanning calorimeter (DSC, Shimadzu DSC-60) was employed to study the thermal transition behavior of s-DFBP-HFDP and its composite membranes. The sample was heated under nitrogen from room temperature to 250°C at 10°C min⁻¹. The thermal stability of the composite membranes was investigated by means of a thermogravimetric analyzer (TGA, Shimadzu DTG-60) from 50 to 600°C at a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. The ionic conductivities of composite membranes were calculated from the bulk sample impedances in the frequency range of 100 Hz to 300 kHz range at zero-phase angle. Electrochemical impedance measurements

were performed by a frequency response analyzer (FRA, PARSTAT 2273) and a conductivity cell containing two stainless steel blocking electrodes was used. The cross section of membrane electrode assembly (MEA) was investigated by a scanning electron microscope (SEM, Hitachi S-2600H).

2.4. Preparation of MEA and Single Cell Test

The single cell test was carried out employing GDE with Pt/C catalyst (E-TEK, ELAT, Pt loading of 0.5 mg cm^{-2}). The ionic liquid was impregnated by brushing on the surface of GDE to improve the electrochemical contact between the electrodes and the composite membrane. The membrane electrode assembly (MEA) was prepared by pressing the electrode/membrane/electrode sandwich (the geometric electrode area was 5 cm^2) under a pressure of 0.3 MPa at 100°C for 5 min. Dry oxygen and hydrogen, obtained from Japan Air Gas Co. (Purity 99.999%), were flowed by the rate of 30 mL min^{-1} . Single cell tests were performed with the aid of a Hokuto Denko HZ-3000 electrochemical measurement system.

3. Results and Discussion

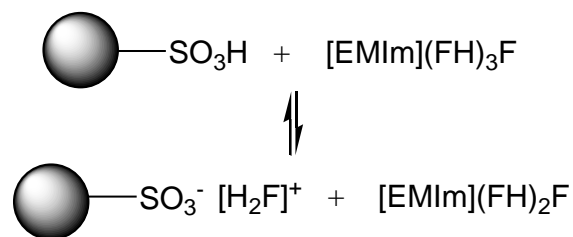
3.1. Thermal Properties

Thermal stabilities of fluorohydrogenate ionic liquid (FHIL) composite membranes were investigated (Table 1, Fig. 1). A weight loss for P(VdF-*co*-HFP) is observed from 310°C and weight losses for s-DFBP-HFDP are observed from 275 and 530°C (Fig. 1 (a) and (b), respectively). These values are similar to those found in the previous report and the weight loss of s-DFBP-HFDP at 275°C is attributed to the elimination of sulfonic acid groups [26]. Decomposition temperatures (T_{Decomp}) of FHIL composite membranes are shown in Fig. 1 (c). Under 100°C, incorporated water within composite membrane was evaporated. At 190-210°C, the second irreversible weight loss occurs and the third weight losses are observed at 270-310°C (Fig. 1 (c)). The second irreversible weight loss is identified as the decomposition of FHIL, the third one is originated from the elimination of sulfonic acid group of s-DFBP-HFDP and the degradation of P(VdF-*co*-HFP) backbone. The decomposition of s-DFBP-HFDP backbone starts lower temperature (at around 450°C) than itself and it might be due to the susceptibility of s-DFBP-HFDP backbone to the decomposed FHIL.

Neat [EMIm](FH)_{2.3}F is thermally less stable than [EMIm](FH)_{1.3}F, releasing HF to become [EMIm](FH)_{*n*}F ($1.3 < n < 2.3$) at lower than 130°C. Interestingly, however, there are no apparent weight decreases observed in this temperature range. Moreover, T_{Decomp} of [EMIm](FH)_{2.3}F and [EMIm](FH)_{1.3}F without s-DFBP-HFDP are around 190 and 210°C, respectively, but in the case of [EMIm](FH)_{2.3}F with s-DFBP-HFDP, T_{Decomp} of [EMIm](FH)_{2.3}F are increased similar to that of [EMIm](FH)_{1.3}F (Table 1). From these results, FHIL is suggested to be stabilized by the interaction with the sulfonate groups in

the polymer. This result is completely different from the previous report using Nafion[®] with [BMIm]OTf (1-butyl-3-methylimidazolium triflate) [27]. In the present case, the sulfonic acid could be transformed into a new acid with generated HF at high temperature (Scheme 1). This gives smaller n of [EMIm](FH) _{n} F than 2.3 and it would cause a superior thermal stability of FHIL at over 130°C.

Scheme 1



The DSC curves (see supporting information) of fluorohydrogenate ionic liquid (FHIL) composite membranes show two endothermic signals at 135 and 205°C corresponding to the melting point (T_m) for P(VdF-*co*-HFP) and the glass transition temperature (T_g) of s-DFBP-HFDP, respectively. The T_m values of P(VdF-*co*-HFP) composite membranes slightly decreased with increasing the amount of FHIL. This might be originated from the change in the solubility of P(VdF-*co*-HFP) to the FHILs at temperatures over 100°C. However, in the case of s-DFBP-HFDP composite membranes, there was no significant difference by the amount of FHIL. Therefore, it is suggested that the sulfonate group of s-DFBP-HFDP enhances the thermal stability of P(VdF-*co*-HFP) by decreasing the effect of FHIL to the solubility of P(VdF-*co*-HFP) even at high temperatures.

Moreover, these values are high enough to endure intermediate temperature operation around 120°C.

3.2. Ionic Conductivities

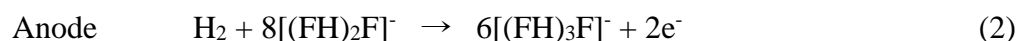
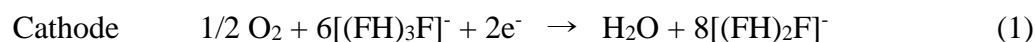
The ionic conductivities of composite membranes were measured. The weight ratio of P(VdF-*co*-HFP) and s-DFBP-HFDP was fixed to 1:0.3 and various amounts of [EMIm](FH)_{*n*}F (*n* = 1.3 and 2.3) were added to make composite membranes.

In general, the ionic conductivity is proportional to the charge carrier density and its mobility. Therefore, the ionic conductivity increases with the increase of the FHIL amount and the elevation of the temperature (Fig. 2): when the ratio of P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F is 1/0.3/1.25, the composite membrane showed ionic conductivities up to 7.2 and 27.4 mS cm⁻¹ at 25 and 130°C, respectively. In the case of 1/0.3/1.75, it exhibits 11.3 and 34.7 mS cm⁻¹ at 25 and 130°C, respectively. These relatively high ionic conductivities of FHIL composite membranes are due to the intrinsic high ionic conductivity of the neat [EMIm](FH)_{2.3}F. However, the FHIL composite membranes containing over twice in the ratio of ionic liquids to polymers could not be obtained. When P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{1.3}F (1/0.3/0.75) is used, the lower ionic conductivity is observed, for example, 2.1 and 11.0 mS cm⁻¹ at 30 and 130°C, respectively. This result is due to not only the small amount of FHIL but also lower intrinsic ionic conductivity of [EMIm](FH)_{1.3}F than that for [EMIm](FH)_{2.3}F. Although the discontinuous change of the ionic conductivity at around $1000/T = 3.1$, namely, $T = \sim 320$ K (50 °C)

observed in the curve (c) is not unambiguously explained now, it might be related to the water incorporation in the membrane at lower temperatures since [EMIm](FH)_{1.3}F is more hygroscopic than [EMIm](FH)_{2.3}F. The FHIL composite membranes containing [EMIm](FH)_{2.3}F are good candidates for PEFC owing to their high ionic conductivities.

3.3. Single Cell Tests of Composite Membranes

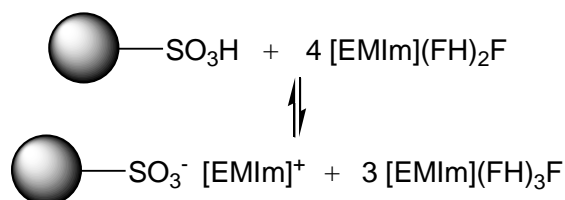
The electrode reactions of the FHFC operation has been reported elsewhere [24]. The cathode, anode and total reactions for the [EMIm](FH)_{2.3}F fuel cell are:



This fuel cell does not require water supply for the electrode reaction or humidification of the electrolyte [24]. In addition, to improve the immobilization of ionic liquids within the polymeric matrix, we introduced partially sulfonated-fluorinated poly(arylene ether) as a functional polar region of which sulfonic acid group was expected to interact with the cation of the ionic liquids. The sulfonic acid might be exchanged with fluorohydrogenate

anion and could form new ion pair with imidazolium (Scheme 2) as in the case of [BMIm][CS] (1-butyl-3-methylimidazolium camphorsulfonate) [28].

Scheme 2



In order to operate a PEFC, the polymer electrolyte membrane should have high ionic conductivity, mechanical strength, and thermal stability. Some of the FHIL composite membranes exhibit high conductivity values over 30 mS cm^{-1} when they are mixed with a large amount of FHIL, however, excess FHIL resulted in a low mechanical strength which is unsuitable for the PEFC operation. Moreover, when the ratio of s-DFBP-HFDP increases, it is difficult to form a good thin film. Therefore, the single cell test was performed using composite membranes having proper mechanical and thermal strengths without losing a high ionic conductivity. The single cell test was carried out with gas diffusion electrodes with Pt/C catalyst (E-TEK, ELAT, Pt loading of 0.5 mg cm^{-2}). The single cell was fed with dry oxygen and hydrogen at 30 mL min^{-1} at ambient pressure.

Figure 3 shows the open-circuit voltage (OCV) of the fuel cell at 130°C using the composite membrane, P(VdF-co-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.25). The single cell exhibits OCV around 1.0 V, which is slightly lower than the theoretical value of 1.22 V. The observed difference would be due to the gas crossover and the irreversible

cathode reaction. Especially, the OCV is exhibiting approximately 1.0 V without humidification at 130°C for over 5 h. Figure 4 shows current-voltage and current-power curves of the single cell using P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1.0/0.3/1.75) under dry H₂ and O₂ flow at 120°C. The maximum power density so far obtained is 20.2 mW cm⁻² at 60.1 mA cm⁻². Although a potential drop increasing with the current density is probably due to the cathodic polarization and to some extent to IR drop, this result shows the availability of FHIL composite membranes as the polymer electrolyte membranes for unhumidified fuel cells operating at middle ranged temperatures.

When the cross section of MEA was investigated by SEM, good-contact between GDEs and an FHIL composite membrane was observed, even after the operation of the fuel cell at 120°C without humidification (Fig. 5). While the thermal stability of s-DFBP-HFDP is strong enough to endure at this temperature, the relatively low melting temperature of P(VDF-*co*-HFP) when it is mixed with FHIL seems to improve the adhesion between GDEs and the membrane.

4. Conclusions

Novel composite electrolyte membranes consisting of [EMIm](FH)_{*n*}F (*n* = 1.3 and 2.3) and fluorinated polymers have been prepared and their physical and electrochemical properties have been studied. Polar sulfonate groups are introduced to the polymer to immobilize FHIL within polymeric matrix. These fluorohydrogenate ionic liquid-based composite membranes showed enough thermal stabilities to operate at temperatures over

100°C. The ionic conductivities of the composite membrane (P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75)) are 11.3 and 34.7 mS cm⁻¹ at 25 and 130°C, respectively. The OCV for the single cell using the composite membranes is ~1.0 V under dry hydrogen and oxygen flows at 130°C for over 5 h. The maximum power density achieved is 20.2 mW cm⁻² at 60.1 mA cm⁻² at 120°C. From their good physical and electrochemical properties, the FHIL composite membranes has been proved to be a promising candidate for the electrolytes of unhumidified fuel cells operating at intermediate temperatures.

Acknowledgments

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Table 1

Thermal properties of several ionic liquid composite membranes

Fig. 1. TGA curves for (a) P(VdF-*co*-HFP), (b) s-DFBP-HFDP, and (c) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75).

Fig. 2. Ionic conductivities of FHIL composite membranes as a function of temperature.

(a) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.25), (b) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75), (c) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{1.3}F (1/0.3/0.75).

Fig. 3. OCV of the single cell using FHIL composite membrane (P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.25)) under dry H₂ and O₂ flow at 130°C.

Fig. 4. Current-voltage and current-power curves of the single cell using FHIL composite membrane (P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75)) under dry H₂ and O₂ flow at 120°C.

Fig. 5. SEM micrograph of MEA by using P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75) after the operation of fuel cell at 120°C without humidification.

Table 1

Thermal properties of several ionic liquid composite membranes

P(VdF- <i>co</i> -HFP)/s-DFBP-HFDP/[EMIm](FH) _n F (<i>n</i>)	<i>T</i> _m (°C)	<i>T</i> _{Decomp} (°C)
P(VdF- <i>co</i> -HFP)	160	310
1/0/1 (2.3)	138	192 ^b , 274
1/0/1.75 (2.3)	127	194 ^b , 276
1/0/ 1 (1.3)	132	210 ^b , 292
1/0/1.5 (1.3)	131	211 ^b , 286
1/0/2 (1.3)	122	209 ^b , 284
s-DFBP-HFDP (10/4h)	205 ^a	275 ^c , 530
s-DFBP-HFDP (20/4h)	206 ^a	280 ^c , 534
1/0.3/1.25 (2.3)	135, 204 ^a	208 ^b , 281 ^c , 438
1/0.3/1.75 (2.3)	134, 205 ^a	209 ^b , 279 ^c , 436

^a *T*_g of s-DFBP-HFDP.

^b *T*_{Decomp} of FHILs.

^c *T*_{Decomp} of sulfonate group.

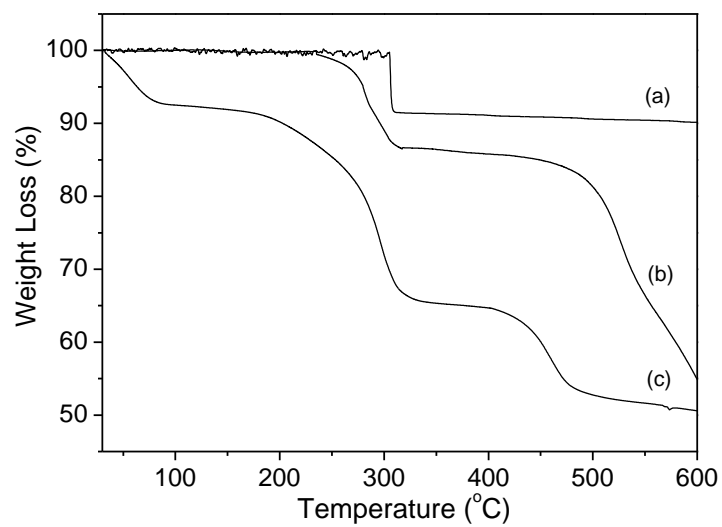


Fig. 1. TGA curves for (a) P(VdF-co-HFP), (b) s-DFBP-HFDP, and (c) P(VdF-co-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75).

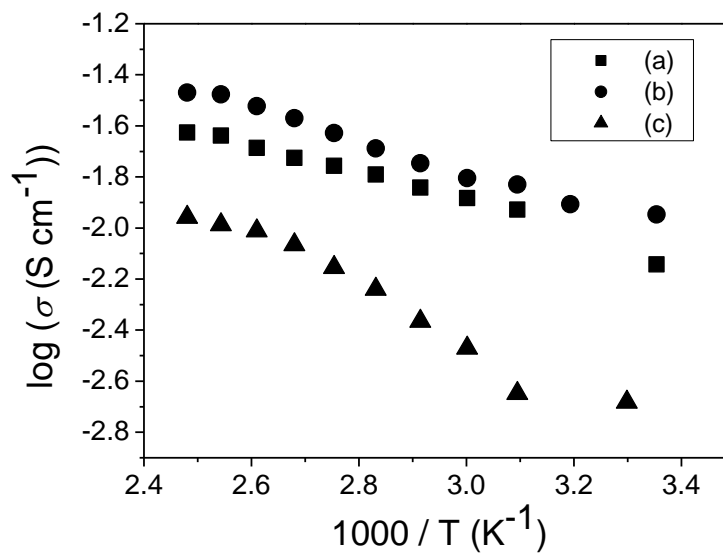


Fig. 2. Ionic conductivities of FHIL composite membranes as a function of temperature.

(a) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.25), (b) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.75), (c) P(VdF-*co*-HFP)/s-DFBP-HFDP/[EMIm](FH)_{1.3}F (1/0.3/0.75).

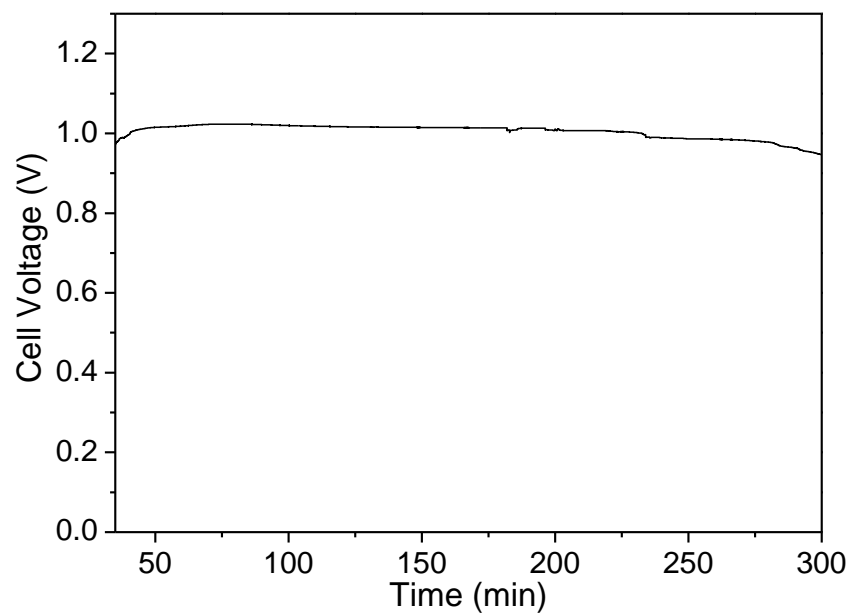


Fig. 3. OCV of the single cell using FHIL composite membrane (P(VdF-co-HFP)/s-DFBP-HFDP/[EMIm](FH)_{2.3}F (1/0.3/1.25)) under dry H₂ and O₂ flow at 130°C.

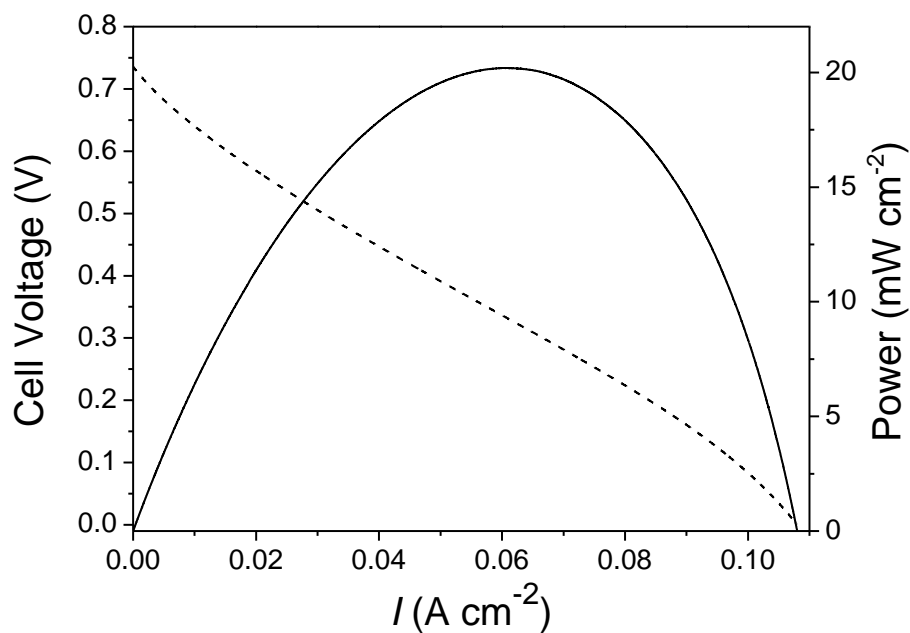


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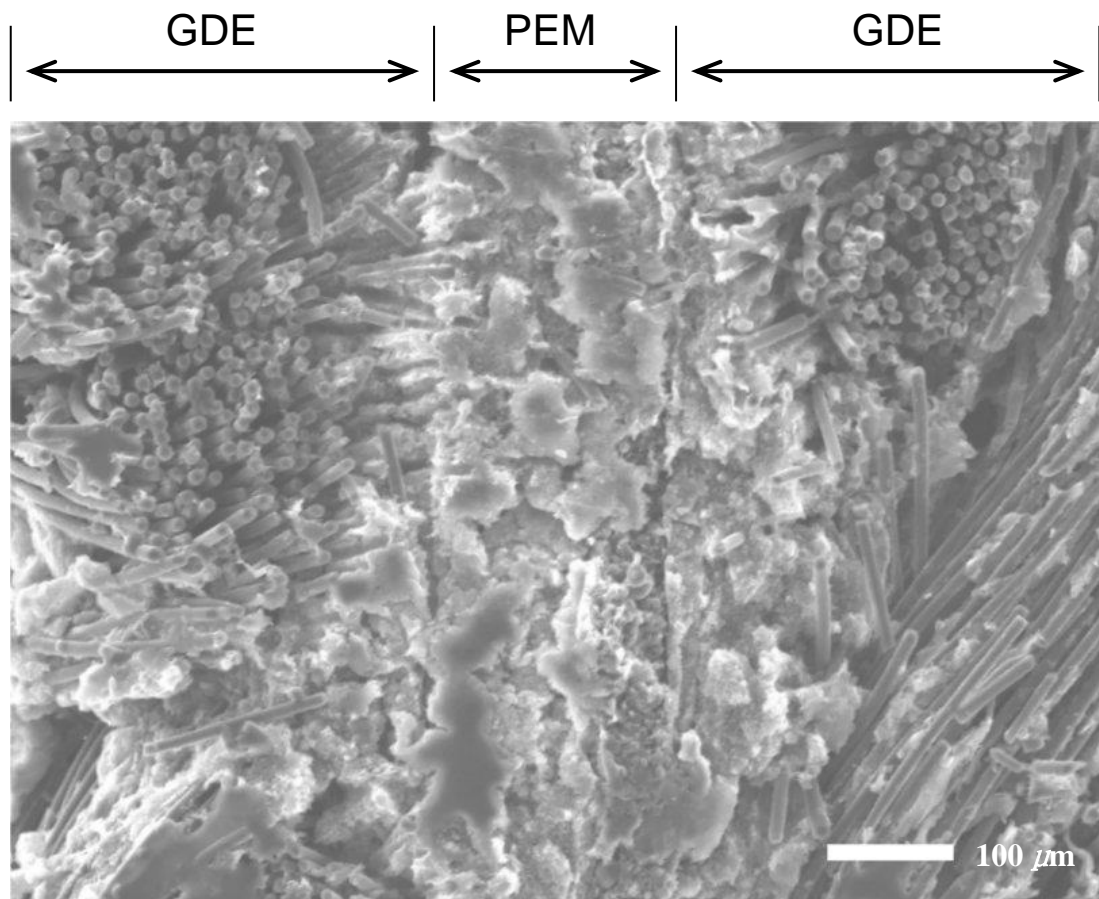


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