Ionic Liquid Fluorohydrogenates and Their Applications

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The recent results are described on the developments of ionic liquid (IL) fluorohydrogenates with high ionic conductivities and wide electrochemical windows. Several cyclic ammonium cations have been found to be combined with fluorohydrogenate anions giving a vacuum stable ionic liquid fluorohydrogenates, $Cat^+[(FH)_{2.3}F]^-$. N-ethyl-N-methylpyrrolidinium fluorohydrogenate, $EMPyrro(FH)_{2.3}F$, and N-allylpyridinium fluorohydrogenate, $APyrid(FH)_{2.3}F$, exhibit wide electrochemical windows compared to the other fluorohydrogenates. A fluorohydrogenate fuel cell (FHFC) using HF-deficient IL, 1-ethyl-3-methyl-imidazolium fluorohydrogenate, $EMIm(FH)_{1.3}F$, as the electrolyte operates at 120°C without humidification. The maximum output power so far obtained in the preliminary cell test is 41 mWcm^{-2} (0.41 V and 100 mA cm^{-2}) at 40°C without humidification.

New cations for ionic liquid fluorohydrogenates, $Cat^+[(FH)_{2.3}F]^-$

We have recently found that, in addition to imidazolium cations, some quaternary ammonium cations shown in Fig. 1 form vacuum stable room temperature ionic liquid (IL) fluorohydrogenates, $Cat^+[(FH)_{2.3}F]^-$. These salts possess high conductivity and excellent stability at ambient conditions. They are all heterocyclic cations combined with
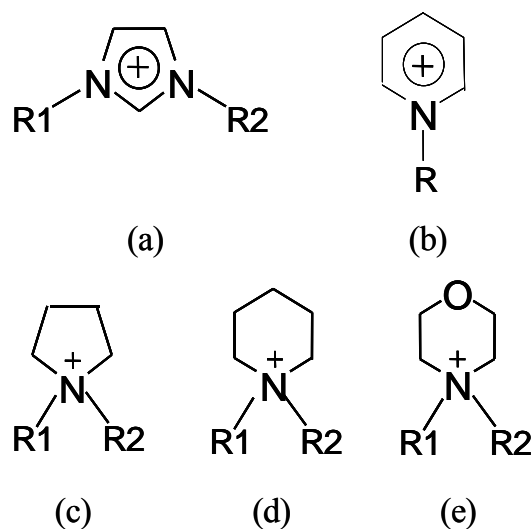

Figure 1. Cations combined with fluorohydrogenate anions to form ionic liquid fluorohydrogenates. (a)1,3-dialkylimidazolium, (b)N-alkylpyridinium, (c)N,N-dialkylpyrrolidinium, (d)N,N-dialkylpiperidinium, (e) N,N-dialkylmorphornium.

fluorohydrogenate anions. All of them exhibit the same vacuum stable composition, $Cat^+[(FH)_{2.3}F]^-$, at room temperature regardless of the type of the cation. The non-integer figure of 2.3 occurring in the formula is due to the mixing of two types of fluorohydrogenate anions, $[(FH)_2F]^-$ and $[(FH)_3F]^-$ (1-3).

A high conductivity of 100 mS cm^{-1} is found for 1-ethyl-3-methylimidazolium fluorohydrogenates (1). The electrochemical window of the salt is approximately 3 V, not wide enough for application to advanced capacitors (4). As a result of systematic survey of cations, we have found some ammonium cations that exhibit superior electrochemical stability without losing conductivities when they are combined with fluorohydrogenate anions (Table 1). Among the ionic liquid fluorohydrogenates synthesized so far, *N*-ethyl-*N*-methylpyrrolidinium fluorohydrogenates, EMPyrro(FH)$_{2.3}$F, and *N*-allylpyridinium fluorohydrogenate, APyrid(FH)$_{2.3}$F, exhibit wide electrochemical windows compared to the other fluorohydrogenates as well as high ionic conductivities of around 80 mScm^{-1}(2,3).

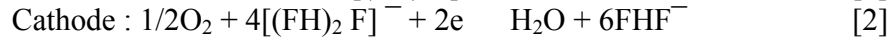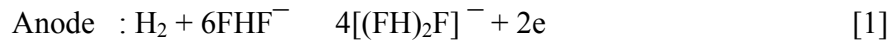**Fluorohydrogenate fuel cells operating at middle-ranged temperatures without humidification**

One of the unique applications of the IL fluorohydrogenates is the electrolyte for a fuel cell operating at middle-ranged temperatures (100-150°C) without humidification of the

TABLE 1 Some physical properties of ionic liquid fluorohydrognates*.

IL fluorohydrogenates	Density d/g cm^{-3}	Viscosity η/cP	Conductivity σ/mScm^{-1}
DMIm(FH)$_{2.3}$F	1.17	5.1	110
EMIm(FH)$_{2.3}$F	1.13	4.9	100
AMIm(FH)$_{2.3}$F	1.11	5.5	90
PrMIm(FH)$_{2.3}$F	1.11	7.0	61
BMIm(FH)$_{2.3}$F	1.08	19.6	33
PeMIm(FH)$_{2.3}$F	1.05	26.7	27
HMIm(FH)$_{2.3}$F	1.00	25.8	16
AMPyrro(FH)$_{2.3}$F	1.05	8.5	78
EMPyrro(FH)$_{2.3}$F	1.07	9.9	74.6
PrMPyrro(FH)$_{2.3}$F	1.05	11.2	58.1
BMPyrro(FH)$_{2.3}$F	1.04	14.5	35.9
HeMPyrro(FH)$_{2.3}$F	0.993	18.0	23.7
AMPip(FH)$_{2.3}$F	1.06	16.7	63
EMPip(FH)$_{2.3}$F	1.07	24.2	37.2
PrMPip(FH)$_{2.3}$F	1.06	33.0	23.9
BMPip(FH)$_{2.3}$F	1.04	37.1	12.3
APyrid(FH)$_{2.3}$F	1.12	5.3	82
BPyrid(FH)$_{2.3}$F	1.09	25.0	37
AMMor(FH)$_{2.3}$F	1.16	34.6	35

*At 298K. Abbrev.; Im:imidazolium, Pyrro: pyrrolidinium, Pip: piperidinium, Pyrid: pyridinium, Mor: morphornium, DM: dimethyl, E: ethyl, M: methyl, Pr: propyl, B: butyl, Pe: pentyl, H: hexyl, A: allyl.

electrolyte (5), taking advantage of their non-volatile nature and high conductivity in addition to the ability of proton transport via the fluorohydrogenate anions. HF-deficient and thermally more stable ionic liquid fluorohydrogenate, $EMIm(FH)_{1.3}F$ (6), is applied for the cell operation at more than 100°C (Fig. 2). The cell operation has been confirmed using a neat fluorohydrogenate as a liquid electrolyte. The conceivable electrode reactions are as follows.

$$\text{Anode} \quad : H_2 + 6FHF^- \quad 4[(FH)_2F]^- + 2e \qquad [1]$$
$$\text{Cathode} : 1/2O_2 + 4[(FH)_2 F]^- + 2e \quad H_2O + 6FHF^- \qquad [2]$$
$$\text{Total} \quad : H_2 + 1/2O_2 \quad H_2O \qquad [3]$$

For practical operation of the cell, the IL is immobilized in a polymer matrix that is sandwiched between the gas diffusion electrodes to form a membrane-electrode assembly (MEA). Fluorohydrogenates are mixed with some monomers (7) or polymers dissolved in some organic solvents (8) and the composites are formed by polymerization or elimination of the organic solvents. In the present study, hydroxylethyl methacrylate (HEMA) was used as a monomer to be mixed with the IL. Figure 3 shows the ionic conductivities of the composites under dry hydrogen atmosphere. The conductivity of the neat IL-HEMA polymer composite fixed in a porous PTFE membrane (thickness: 80 μm, vacancy ratio: 80%, diameter: 0.45 μm) is decreased with the increase of the polymer content in the membrane. The ionic conductivity of the composite made from the equimolar mixture of the IL and HEMA monomer exhibits 45 mS cm^{-1} at 120°C. Figure 4 shows a TG curve of the IL-HEMA polymer composite (5:5) fixed in the PTFE membrane. The weight decrease at around 270°C is ascribed to the thermal decomposition of the IL. A slight weight decrease found in the temperature range of 100 to 200°C is mostly ascribed to the water elimination from the composite. Partial decomposition of the anions of the IL would contribute to the weight loss but not for the temperatures of lower than 130°C since the $EMIm(FH)_{1.3}F$ is prepared by thermal decomposition of $EMIm(FH)_{2.3}F$ at 130°C and stable at this temperature.

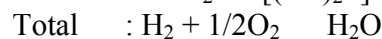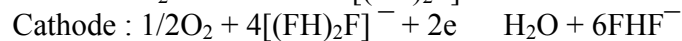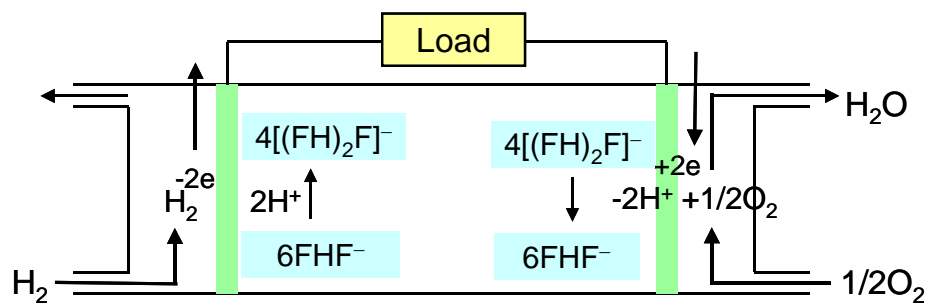Usually the liquid mixture is soaked in a porous plastic film before polymerization

$$\text{Anode} \quad : H_2 + 6FHF^- \quad 4[(FH)_2F]^- + 2e$$
$$\text{Cathode} : 1/2O_2 + 4[(FH)_2F]^- + 2e \quad H_2O + 6FHF^-$$
$$\text{Total} \quad : H_2 + 1/2O_2 \quad H_2O$$

Figure 2. Fluorohydrogenate fuel cell (FHFC). The electrode reactions described are for EMIm(FH)$_{1.3}$F in which the major anionic species are FHF$^-$ and [(FH)$_2$F]$^-$.
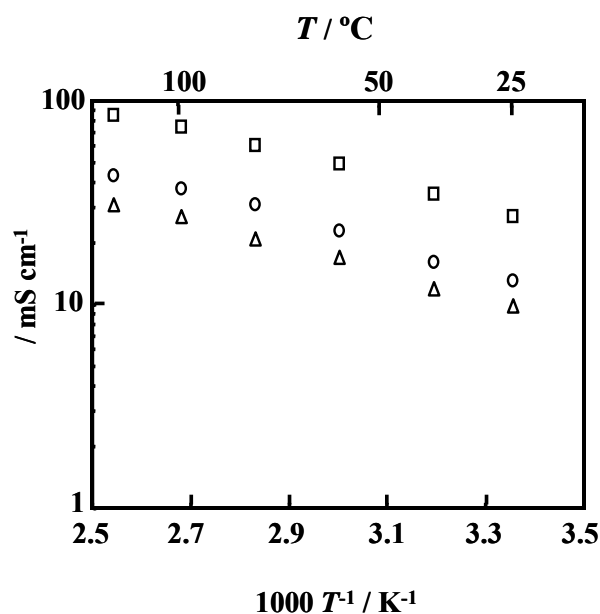

Figure 3. Ionic conductivity of EMIm(FH)$_{1.3}$F-HEMA composite fixed in a porous PTFE membrane (Thickness: 80 μm, Vacancy ratio: 80 %, diameter: 0.45 μm). □: neat EMIm(FH)$_{2.3}$F, ○: 5:5, △: 4:6 in molar ratio.
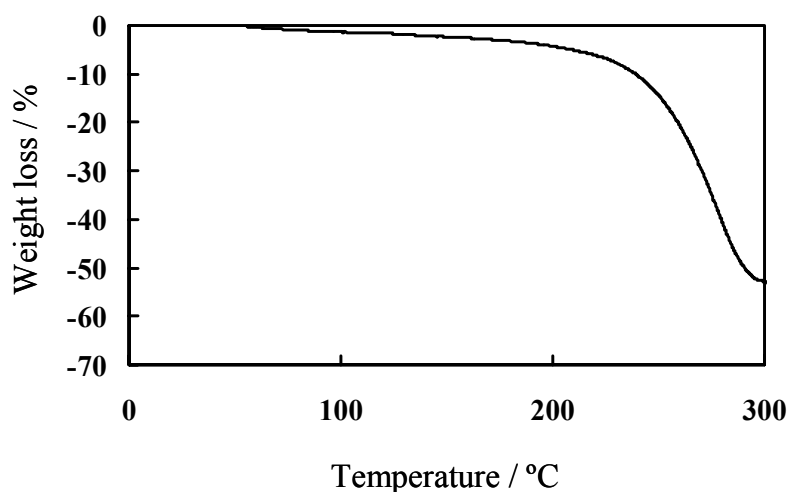

Figure 4. TG curve of EMIm(FH)$_{1.3}$F-PolyHEMA (5:5) composite membrane on GDE under N$_2$ atmosphere. Scanning rate: 10°C min^{-1}, N$_2$ flow rate: 200 ml min^{-1}.

in order to provide enough mechanical strength to the composite membranes. The membrane is sandwiched between the gas diffusion electrodes (GDE, E-TEK, ELAT®) with a geometrical surface area of 5 cm^2. Pt catalyst of 5.0 mg cm^{-2} for both the H$_2$ anode

and O_2 cathode is fixed on the GDE without using Nafion® glue. Figure 5 shows a schematic illustration of the test cell. The separators are carbon blocks with serpentine flow channels. The cell is equipped with a reference hydrogen electrode made of a platinum wire that is placed in the hydrogen flow channel, the tip contacting the electrolyte membrane.

Figures 6 and 7 show I-V (diamond) and I-P plots (circle) of the cell operating at 40ºC
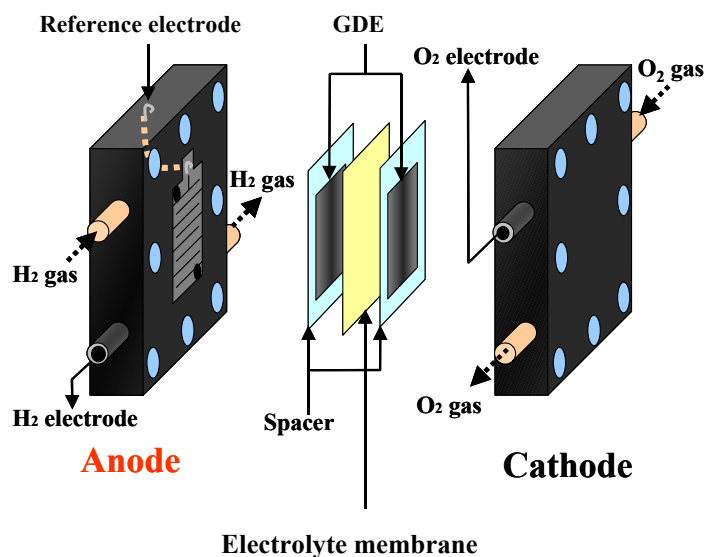

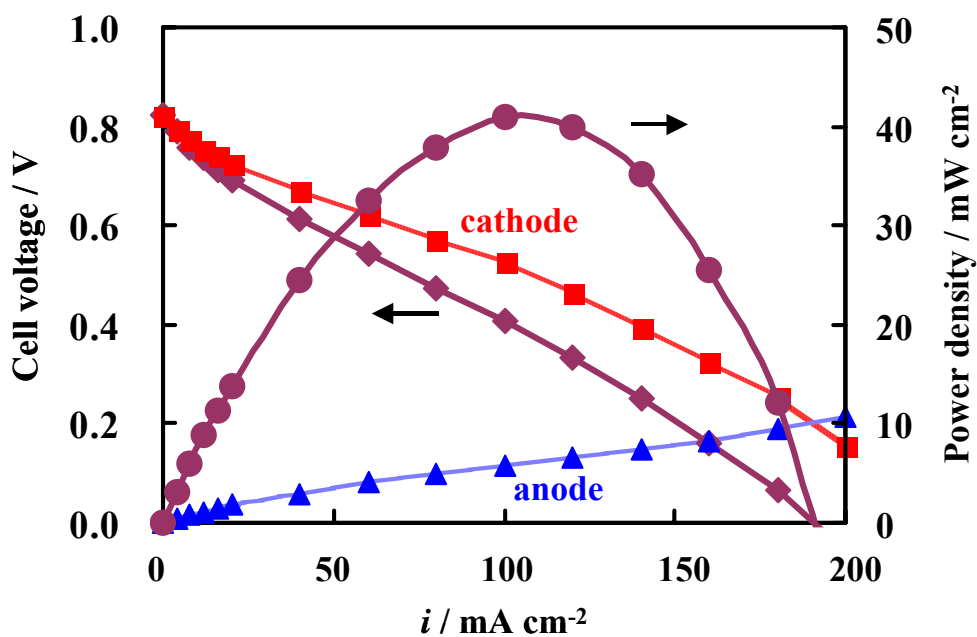Figure 5.   A schematic illustration of the test cell.

Figure 6. I-V and I-P plots of FHFC operating at 40ºC without humidification. H_2 and O_2 flow rate: 25 ml min^{-1}. EMIm(FH)$_{1.3}$F:2-hydrogxyethyl methacrylate = 1:1(in molar ratio).
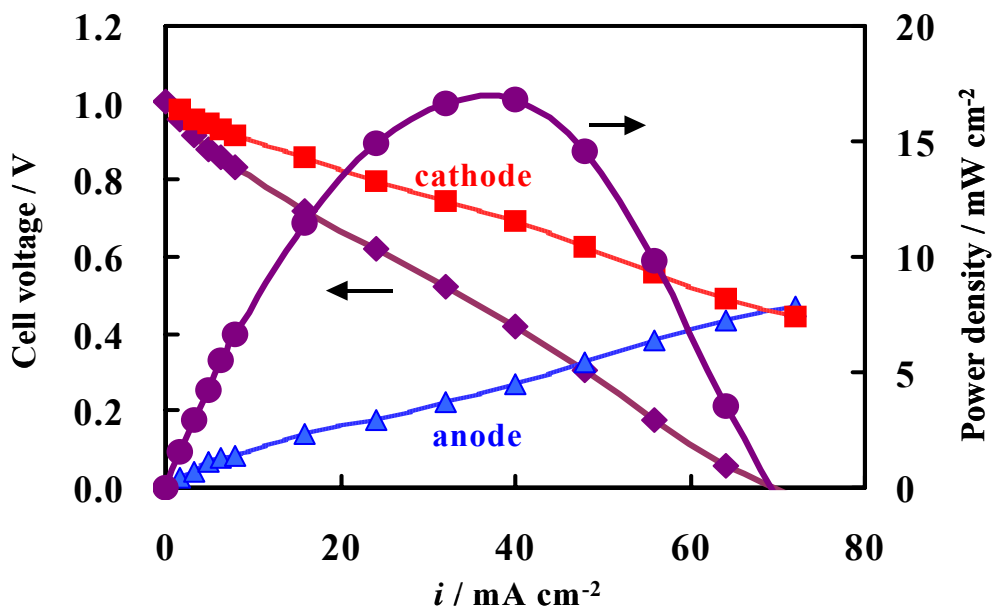

Figure. 7. I-V and I-P plots of FHFC operating at 120ºC without humidification. H_2 and O_2 flow rate: 25 ml min^{-1}. EMIm(FH)$_{1.3}$F:2-hydrogxyethyl methacrylate = 1:1(in molar ratio).

120ºC without humidification, respectively. Plots of cathode (square) and anode (triangle) polarization measured against the reference hydrogen electrode are also included in the figures. The highest output power of 41 mW cm^{-2} was obtained (0.41 V and 100 mA cm^{-2}) at 40ºC. In addition to the cathode overpotential, the anode overpotential of this fuel cell is fairly large compared to that found for the PEMFC anode. When the cell operated at 120ºC, both the cathode and anode overpotentials were increased to decrease the maximum output power down to 17 mW cm^{-2} (0.42V and 40 mA cm^{-2}). Especially the increase of the anode overpotential is significant compared to that of the cathode. As shown in eq. 1, the anode reaction of this FHFC is considered to involve the transformation of fluorohydrogenate anions with the reaction with hydrogen, which is different from the conventional PEMFC. However, the unexpected increases of the overpotentials of both the electrodes by the elevation of operation temperature found in the present study is presumably due to the decrease of the effective reaction interface between the membrane and GDE by the deformation of the polymer composite membrane. The search for thermally more stable polymer to be combined with the IL is necessary for further improvement of the cell performance of the FHFC.

Conclusions

Ionic liquid fluorohydrogenates vacuum-stable at ambient temperature giving an identical composition, $Cat(FH)_{2.3}F$, are formed by the combination with some cyclic onium cations. A wide electrochemical window of more than 4 V is realized by the choice of cation and the alkyl group on it. A fluorohydrogenate fuel cell (FHFC) operates at middle-ranged temperatures of more than 100ºC under non-humidified conditions. Further developments of the polymer-IL composite electrolytes, gas diffusion electrodes and catalysts are necessary for the improvement of the cell performance.

Acknowledgments

References

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