New Electrolyte Materials for Fuel Cells

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Hydrogen is a medium for energy storage and delivery. In a hydrogen energy system, the enhancement of the energy efficiency for conversion from the chemical energy of hydrogen to electricity is one of the most important key factors to make the system highly efficient, considering in particular the fact that electricity is the highest quality form of energy. Therefore, fuel cell systems are a key technology for the hydrogen energy system, because they directly convert chemical energy to electric energy with expected high theoretical conversion efficiency. For thermal engines, on the other hand, the chemical energy of fuel converts to mechanical energy through thermal energy, with the thermodynamic conversion efficiency limit imposed by the Carnot efficiency. In fuel cells, the energy conversion proceeds electrochemically and its process is free from the Carnot efficiency limit. Although fuel cells have potential for much higher theoretical efficiency than thermal engines, there remain important technical problems for achieving such high efficiency as well as cost issue.

A fuel cell consists of an electrolyte and two electrodes. The electrolyte layer is placed between two gas-diffusion electrodes. The electrolyte layer works as an ionic conductor and a gas separator fuel and oxidant gases. The reactions of fuel cell with acid electrolyte are as follows.

[Anode: oxidation] $H_2 \rightarrow 2H^+ + 2e^-$

[Cathode: reduction] $1/2\ O_2 + 2H^+ + 2e^- \rightarrow H_2O$

[Total: combustion] $H_2 + 1/2\ O_2 \rightarrow H_2O$

The theoretical efficiency of fuel cells is given by [Gibbs free energy]/[Enthalpy], which is ca. 83% in ambient temperature operation. The types of fuel cells depend on the electrolyte material used; such as phosphoric acid, molten carbonate, solid oxide and polymer electrolyte. Also, the working temperature depends on the electrolyte material. The characteristics of the fuel cells are shown in table 1.

Recently, polymer electrolyte fuel cells (PEFCs, so called proton exchange membrane fuel cell (PEMFC)) have been developed as an electric power unit for electric vehicles and co-generation systems (simultaneous generation of heat and power) for the residential use. The advantages of PEFCs when compared with other types are their high power density and easy-to-control characteristics. The advantages and disadvantages of PEFC are as follows.

Table 1 Characteristics of fuel cells.

	PEFC	PAFC	MCFC	SOFC
electrolyte	PEM (proton exchange membrane)	phosphoric acid (98% H_3PO_4)	molten carbonate $(Li/Na)_2CO_3$	zirconia (stabilized ZrO_2)
carrier	H^+	H^+	CO_3^{2-}	O^{2-}
electrode (Anode-Cathode)	Pt/C - Pt/C	Pt/C - Pt/C	Ni alloy - NiO	Ni/stabilizedZrO2 - Conductive oxide
temperature	80℃	200℃	650℃	1000℃
fuel	H_2 (CO<50ppm)	H_2 (CO<2%)	H_2,CO,(CH_4)	H_2,CO,CH_4
current density	1A/cm^2	0.3A/cm^2	0.15A/cm^2	0.3A/cm^2

[Advantages]

- High power density in comparable to those of internal combustion engines
- Easy to start up from ambient temperature condition
- Easy to control (e.g. structural reliability of membrane to withstand the pressure difference between H_2 and O_2 gas channels, etc.)

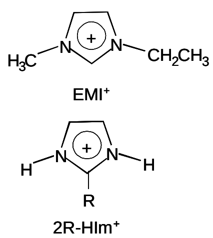
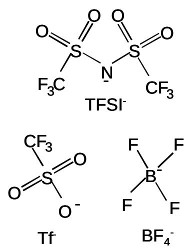
[Disadvantages]

- Relatively low energy conversion efficiency due to large efficiency loss occurred in the kinetics of O_2 reduction reaction
- High Pt catalyst loading at electrodes
- Water management to maintain the ionic conductivity of electrolyte and gas diffusivity in the electrodes; i.e. humidity control for H_2 and O_2 is essential.

These characteristics originate from the property of the proton exchange membrane, which is highly ionic conductive under hydrated condition. That is, water absorption is essential to maintain proton conduction because proton conducts by hopping among water molecules.

If we have a proton conductive membrane that works in mesothermal condition, or conditions at a temperature range of 100-150 ^oC, with low humidity, the operation temperature of fuel cell can be increased so that the reaction kinetics can be promoted and easy water management becomes feasible. To achieve proton conduction under the mesothermal condition, one way is to keep water within membrane molecular structure by a strong acid, and the other way is to find out alternative proton conductive medium. In this presentation, we focus our attention on RTMSs (room temperature molten salts) as a proton conduction medium. The example of the chemical structures is shown in table 2. RTMS is also called "Ionic liquid", and liquid without any solvent. The characteristics of RTMS are as follows.

Table 2 Chemical structures of RTMSs.

Cation	Anion
 EMI$^+$, 2R-HIm$^+$ (R: alkyl group, Me: methyl, Et: ethyl, Pr: propyl, or H)	 TFSI$^-$, Tf$^-$, BF_4^-

- High ionic conductivity
- Very low vapor pressure and high thermal stability
- High chemical and electrochemical stability

Our research group has proved that the 2R-HIm$^+$ (2-alkile- imidazolium cation) and the acid added EMI$^+$ (1-ethyl- 3-methyl- imidazolium cation) type (see table 2) show potential as highly proton conductive media. They are stable over 200 ^oC and show relatively high ionic conductivities even under dry atmosphere. Their conductivities are measured as ca. 10^{-1} S cm^{-1} for liquid and ca. 10^{-3} S cm^{-3} for RTMS absorbed membrane at around 130^oC. We have already verified fuel cell operation by using these unique materials successfully and are currently improving the gas diffusion electrodes.

Key words:

Mesothermal: "Mesothermal" implies the temperature range form 100 to 150 ^oC.

Electrolyte membrane: High ionic and low electronic conductive material for electrochemical systems. The membrane also works as a separator of fuel and oxidant gas for fuel cells.

Gas diffusion electrode: A kind of porous structured electrode where the gas diffusivity, ionic conductivity and electronic conductivity are optimally controlled.