Proton-conducting ionic liquids based upon multivalent anions and alkylimidazolium cations

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Alkylimidazolium type ionic liquids have been prepared with acidic anions derived from multivalent anions with the expectation of excellent thermal properties and ionic conductivity, including proton conduction.

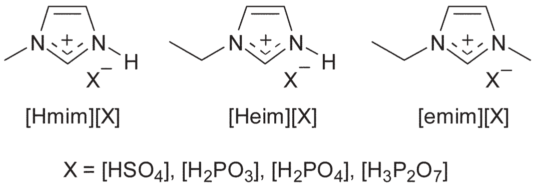
Polymer electrolyte type fuel cells (PEFCs) are expected to be inevitable energy conversion devices for vehicles or portable electronic devices because PEFCs have characteristics such as good power generation efficiency, high power density and they perform well at ambient temperatures.[1,2] PEFCs have been composed of fluorinated polymer electrolytes containing water. Fast proton conduction in the polymer electrolyte membranes obeys the Grotthus mechanism due to successive hydrogen bonding of water molecules. Since ion conduction in the polymer electrolytes strongly depends on the water content,[3] the conductivity decreases with evaporation of the water above 100 °C or freezing below 0 °C.[4] This restricts the application temperature of PEFCs from room temperature to 130 °C even if hydrous gases are pressurised. For actual utilisation, however, PEFCs must be able to be operated in a temperature range from below subfreezing temperature to over 200 °C. Expansion of the operational temperature range is needed not only to expand the application of PEFCs but also to achieve a simplification of the PEFC power generation system, a higher efficiency of power generation, and lower cost.[5] Thermally stable anhydrous proton conductors are expected to replace aqueous conductive materials for PEFCs in operation over 100 °C. There have been several reports about thermally stable anhydrous proton conductors such as inorganic solid acids,[6] azole compounds[4,7] and ionic liquids (ILs) which are liquid salts at room temperature.[8]

ILs have several unique properties and are known to be novel electrolytes and reaction media. The thermal stability and non-volatility of ILs meet a requirement of the proton conductor for the PEFCs operated at moderate temperatures between 100 and 200 °C. Good ionic conductivity is also an advantage for the anhydrous proton conductor of PEFCs. However, simple ILs such as 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) amide ([emim][NTf_2]) or 1-ethyl-3-methylimidazolium tetrafluoroborate ([emim][BF_4]) are not suitable as proton conductors in spite of their high ion content and good ionic conductivity, because there is no mobile proton or proton accepter/donor site in the salt structure. In order to use ILs as proton conductors, some structural designs have been reported, using acid–base complex type ILs prepared by the neutralisation of amines with strong acids,[9] by addition of acid to known ILs[10] and by the incorporation of ILs into fluorinated polymer electrolytes.[11] On the other hand, our group has prepared ILs containing the small target ions required for electrochemical devices such as a lithium ion battery by using a multivalent anion.[12] In general, ILs are composed of an onium cation and a monovalent anion such as BF_4^-, PF_6^-, $CF_3SO_3^-$ and NTf_2^-. Specific small cations such as a proton or lithium cation can be introduced into the IL structure as components of the anion like hydrogensulfate anion and lithiumsulfate anion. In this work, we have prepared ILs from the combination of imidazolium cations and anions that themselves can dissociate to release proton. The prepared proton-conducting (or proton-containing) ILs (PCILs) have been characterised by their electrochemical and thermal properties.

In this study, 1-methylimidazolium ($Hmim^+$), 1-ethylimidazolium ($Heim^+$) and $emim^+$ cations are used to prepare target ILs. The PCILs were prepared by the neutralisation of tertiary amines and multivalent acids or the anion exchange of [emim]Br by using silver(I) oxide according to the reports.[8,13] Sulfuric acid, phosphorous acid, phosphoric acid and pyrophosphoric acid were used as starting acids.† Structures of the prepared imidazolium salts are shown in Fig. 1.

According to a definition of ILs,[15] salts which melt below 100 °C are categorised as ILs. Except for [Hmim][H_2PO_4], all of the prepared imidazolium salts are ILs, due to their melting point below 80 °C. Thermal properties such as glass transition temperature (T_g), melting point (T_m) and decomposition temperature (T_d) of the imidazolium salts are shown in Table 1. Phase transition temperatures of the prepared imidazolium salts depend on the ion species. The glass transition temperature of the hydrogensulfates especially is lower than that of other salts. It is clear from Table 1 that dihydrogenphosphates have a relatively high phase transition temperature among the salts prepared in this work. The difference of phase transition temperature is considered to be attributable to the dissociation degree of the anion.

Excellent thermal stability of ILs is an essential requirement for highly reliable electrolytes. However, there are not so many ILs



X = [HSO_4], [H_2PO_3], [H_2PO_4], [$H_3P_2O_7$]

Fig. 1 Structure of proton conductive ionic liquids composed of three kinds of imidazolium cations and acidic anions.

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Table 1 Glass transition temperature, melting point, thermal decomposition temperature and ionic conductivity at room temperature of prepared imidazolium salts

Anion	Cation	T_g/°C[a]	T_m/°C[a]	T_d/°C[b]	σ_i/mS cm^{-1} [c]
HSO_4^-	$Hmim^+$	−99	—	320	6.5
	$Heim^+$	−75	—	200	0.24
	$emim^+$	−94	—	360	4.9
$H_2PO_3^-$	$Hmim^+$	−70	47	122	0.22
	$Heim^+$	−76	53	129	0.33
	$emim^+$	−76	—	276	0.18
$H_2PO_4^-$	$Hmim^+$	57	137	164	5.5×10^{-5}
	$Heim^+$	−49	80	168	1.1×10^{-2}
	$emim^+$	−74	—	170	0.24
$H_3P_2O_7^-$	$Hmim^+$	−40	—	197	7.4×10^{-3}
	$Heim^+$	−42	—	212	2.7×10^{-2}
	$emim^+$	−46	—	346	2.3×10^{-2}

[a] 10 °C min^{-1}. [b] Temperature for 10 wt% weight loss. 10 °C min^{-1} with N_2 flow. [c] At 30 °C. Measured by impedance measurement from 10 Hz to 1 M Hz.[14]

which are stable over 400 °C.[16] Most ILs start decomposing in the range between 200 to 300 °C. The thermal decomposition temperature of the prepared imidazolium salts was measured by using thermogravimetric analysis. Thermal decomposition temperature is defined here to be the temperature when 10% of the weight was lost. From the analysis, the thermal decomposition temperature of PCILs differed with anion species as well as glass transition temperature. Hydrogensulfate and trihydrogenpyrophosphate type PCILs are thermally stable compared with dihydrogenphosphate and dihydrogenphosphite. Angell and co-workers reported that the thermal decomposition temperature of ILs prepared by neutralisation depends on the pK_a value of the starting amines and acids.[17] Better thermal stability of sulfate salts should be attributed to the acidity of sulfuric acid which is stronger than that of the phosphoric acid analogs.

The ionic conductivity of these PCILs at 30 °C is summarised in Table 1. Although the ionic conductivity measured by the AC impedance method contains ion conduction of all mobile ions in the matrix, the obtained data can be used to understand the ion conductive behaviour of these samples. The ionic conductivity of PCILs varies depending upon the structure of the cation and anion. By comparing the effect of $Hmim^+$, $Heim^+$ and $emim^+$, the protonated imidazolium cation is concluded to not always be better than the fully alkylated imidazolium cation. It is easy to prepare protonated imidazolium cations for the PCILs by the neutralisation of *N*-alkylimidazoles and multivalent acids. However, these protonated imidazolium cations were strongly suggested not to contribute to the ionic conductivity. Deprotonation of these protonated imidazolium cations may produce volatile alkylimidazole, suggesting less thermal stability. On the other hand, multivalent anions inherently containing proton(s) are strongly effective for the preparation of ILs for anhydrous proton conductive materials. Accordingly, it is important to compare the characteristics of $emim^+$ salts containing multivalent anions.

Hydrogensulfate type PCILs show better ionic conductivity than that of the phosphate derivatives. The ionic conductivity of ILs is affected by the phase state, ion size, degree of charge delocalization, and so on. The ionic conductivities of the prepared salts are plotted in Fig. 2 as a function of their glass transition temperature. The linear relationship implies that the higher ionic conductivity of the sulfate salts should be attributed to the lower glass transition temperature. A clear relationship between glass transition temperature and ionic conductivity is also observed in the case of ILs based on monovalent ions.

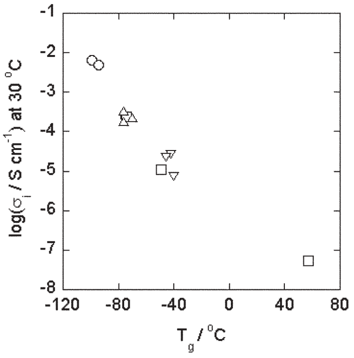

Fig. 2 Relationship between the ionic conductivity at 30 °C and the glass transition temperature for prepared PCILs. HSO_4^- salt (○), $H_2PO_3^-$ salt (△), $H_2PO_4^-$ salt (□), $H_3P_2O_7^-$ salt (▽).

The ionic conductivity of $emim^+$ type PCILs, which showed better thermal stability among the prepared salts, was analyzed to discuss the ion conduction mechanism. Fig. 3 shows the Arrhenius plots of the ionic conductivity of $emim^+$ type PCILs. All plots are on the upper convex curves and obey the Vogel–Fulcher–Tamman (VFT) type temperature dependence behaviour.[17] These results strongly suggested that the ion conduction was based on the migration of the component ions in viscous media and there is no specific contribution from proton transfer such as the proton jump explained by the Grotthus mechanism. The ion conduction as shown in Fig. 3 was analyzed by using the VFT equation ($\sigma_i = AT^{1/2}\exp[-B/(T - T_0)]$).[18] In the equation, parameter A indicates the number of charge carriers, B shows the activation energy for ion conduction of the charge carrier, and T_0 is the ideal glass transition temperature. The T_0 values are 50 K lower than the experimentally-determined glass transition temperature. The ionic conductivity data are shown in Fig. 3 and were substituted into the VFT equation to give linear plots. These results show that the ion conduction in $emim^+$ type PCILs is mainly attributed to the diffusion of carrier ions in viscous media. VFT parameters obtained from the ionic conductivities of the $emim^+$ salts are summarized in Table 2. The ionic conductivity of amorphous materials is proportional to the product of carrier ion number and mobility. If the mobility of the charge carrier in the system obeyed

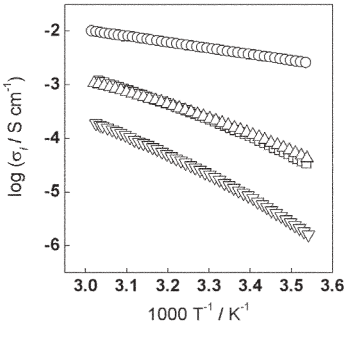

Fig. 3 Temperature dependence of the ionic conductivity for $emim^+$ salt type PCILs analyzed by complex impedance measurements. [emim][HSO_4] (○), [emim][H_2PO_3] (△), [emim][H_2PO_4] (□), [emim][$H_3P_2O_7$] (▽).

Table 2 VFT parameters for ion conduction of emim$^+$ salt type PCILs ($T_0 = T_g - 50$ K)

Anion	A/S K$^{1/2}$ cm^{-1}	B/K	R^2
HSO_4^-	16	916	0.999
$H_2PO_3^-$	222	1705	0.999
$H_2PO_4^-$	661	1859	0.999
$H_3P_2O_7^-$	140	1622	0.999

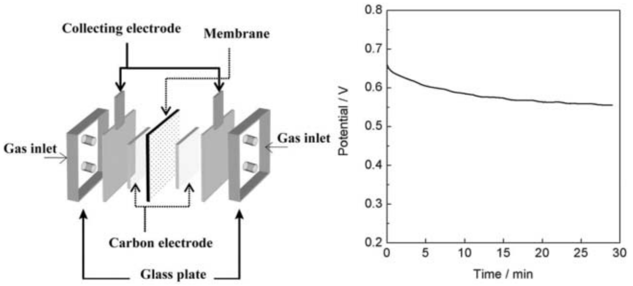

Fig. 4 Right: schematic illustration of the cell used for open circuit voltage measurement. Left: open circuit voltage of the cell composed of an [emim][HSO_4] electrolyte under H_2 and air at room temperature.

only the glass transition temperature, the VFT parameter B should be the same value. [emim][HSO_4] showed a smaller B value than that of other three emim$^+$ salts composed of hydrogenphosphate derivatives. This means that the carrier ions in [emim][HSO_4] move faster than in phosphate type PCILs.

Then we constructed a simple fuel cell with [emim][HSO_4]. The open circuit voltage of the fuel cell was measured to confirm proton conduction. The [emim][HSO_4] was absorbed with 2.2 mm thick cellulose filter to be used as an electrolyte membrane. In addition, [emim][NTf_2] was used as a reference sample. Carbon paper containing 0.5 mg cm^{-2} Pt catalyst (Electrochem. Inc.) was used as a catalyst layer of both anode and cathode. All electrochemical measurements were carried out with an ALS electrochemical analyzer 624B. For open circuit voltage measurements, hydrogen gas was introduced to the anode and air or nitrogen gas was introduced to the cathode. The cell composed of [emim][HSO_4] showed a voltage of *ca.* 0.5 V when hydrogen and air were filled as shown in Fig. 4. The lower voltage than the ideal value was attributed to both the relatively low ionic conductivity compared to that in an aqueous electrolyte and the poor contact between the electrode and electrolyte membrane. When nitrogen gas was introduced into the cathode to remove oxygen, the potential immediately dropped and reduced to zero. On the other hand, the fuel cell composed of [emim][NTf_2] based electrolyte membranes showed no voltage under any gas conditions. Traditional ILs such as [emim][NTf_2], containing no protons, hardly enabled proton transport. Addition of protic compounds as a proton donor and acceptor should be utilized for this purpose. The proton is a very small ion and unstable without suitable carriers.

Novel ILs containing protons, so-called proton-conducting ionic liquids, were designed using multivalent anions and imidazolium cations. These were used to construct anhydrous proton conductors. Among the obtained salts, hydrogensulfate type PCILs showed high ionic conductivity and preferable thermal stability. From the measurement of the open circuit voltage of the cell composed of an [emim][HSO_4] based electrolyte membrane, [emim][HSO_4] was strongly suggested to perform as an anhydrous proton conductor.

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Notes and references

† The starting material, [emim]Br was prepared according to previous work.[8] An aqueous solution of the [emim]Br was slowly mixed with an aqueous solution containing a half molar amount of silver(I) oxide and then the mixture was stirred under dark conditions. After 2 h, a white brown precipitate was removed by filtration. Then it was neutralized with an equimolar amount of multivalent acid. Reaction mixtures were stirred for 12 h at room temperature and then the solution was concentrated with a rotary evaporator. Residual compounds were washed with an appropriate organic solvent to remove unreacted compounds. Residual oils were dissolved in methanol and filtered. After evaporation to remove the methanol, the obtained viscous liquid was dried under reduced pressure at 80 °C. The structure of the obtained compounds was confirmed with ^{1}H NMR.

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