Molecular mobility of imidazoles in molten state as a key factor to enhance proton conductivity

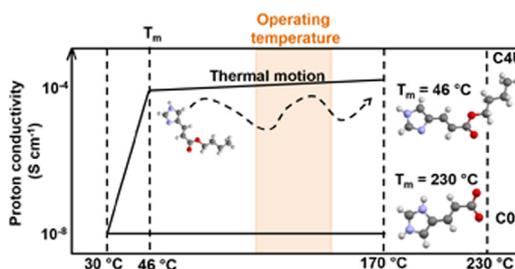Chatchai Jarumaneeroj [a], Kohji Tashiro [b,**], Suwabun Chirachanchai [a,*]

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HIGHLIGHTS

- Alkyl urocanates are a model to represent imidazole with different chain lengths.
- Molecular mobility plays the role in transferring proton under molten state.
- Thermal motion favors the vehicle mechanism in molten state.
- Thermal motion is a key factor to promote proton conductivity.

GRAPHICAL ABSTRACT

ABSTRACT

A systematic study on alkyl urocanates related to the proton conductivity performances to clarify the role of molecular mobility and hydrogen bond in proton transfer is carried out. Depending on the methylene units, the melting (T_m) and degradation temperatures (T_d) change remarkably. When methylene unit is four, **C4U** shows the lowest melting point (as low as 46 °C) and this suggests the favorable molecular mobility in the molten state. The short hydrogen bond distance and the short T_1 relaxation time lead to a scheme of proton conductivity of **C4U** to be under a regular imidazole arrangement with highly active alkyl chain molecular motion. When **C4U** is in molten state, the proton transfer is under vehicle mechanism clarified by Volgel–Tammann–Fulcher (VTF) equation. By applying **C4U** as a proton conductive additive in a sulfonated poly(ether ether ketone) (SPEEK) membrane without any acid dopants, the proton conductivity in the heating process up to 170 °C continuously increases to be $\sim 10^4$ times higher than that of the neat SPEEK. The present work not only demonstrates the thermal mobility as a key factor to govern the proton conductivity but also proposes the effective proton transfer of heterocyclic compounds based on the molten state.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) is an alternative clean energy and can be applied in automobile, portable devices and power generators, etc [1]. Polymer electrolyte membrane (PEM), where proton exchange occurs, is one of the key components in the cell. At present, a series of perfluorosulfonic acid polymers with a good proton conductivity efficiency (10^{-2} S cm^{-1} at 80 °C) are commercially available, e.g. Nafion®, Flemion®, Aciplex®, and Dow®, however, this type of polymer membrane requires water to drive the proton in the form of hydronium ions along the chains [2,3]. The water dehydration limits the PEMFC operation especially at high operating temperature (above 80 °C). The high operating temperature is needed to increase the cell operation efficiency. That is to say, the high operating temperature

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shows its advantage on the removal of CO on Pt catalyst at the electrodes. Then, the high operating temperature becomes an ideal condition [4]. Several approaches, such as composites and nano-composites [5], layer-by-layer [6], coating [7], etc. were proposed as the ways to extend the stability of water clusters in the membrane at the high operating temperature.

Heterocyclic molecules, such as imidazoles, benzimidazoles, pyrazoles, etc. are known to allow the protons to transfer even in the non-aqueous condition [8]. The mechanisms of proton transfer proposed so far were based on an asset of the resonance structure of heterocycles, the proton acceptor of nitrogen atom, the hydrogen bond network, and the molecular reorientation [9]. Up to the present time, the heterocyclic compounds have been introduced in polymer matrices, in the forms of the additives, the blends with heterocyclic polymers, and the copolymers. For example, Bozkurt et al. [10] showed how poly(4,5-vinylimidazole) enhanced the proton conductivity as high as 10^{-4} S cm^{-1} at 150 °C by doping phosphoric acid. Our group found that the copolymer containing proton donor and acceptor of 4,5-vinylimidazole and acrylic acid showed the proton conductivity of 10^{-4} S cm^{-1} at 150 °C [11]. The polymer blends such as poly(acrylic acid) [12], poly(vinyl phos-phonic acid) [13], sulfonated poly(ether ether ketone) (SPEEK) [14,15], Nafion® [4], alginic acid [16], etc. containing heterocyclic compounds showed the proton conductivity of the range of 10^{-4}–10^{-2} S cm^{-1} at above 120 °C.

It is important to note that the heterocyclic molecules, in most cases, exhibit their melting temperature at about 200 °C. Therefore, the operating temperature even as high as 150 °C is still lower than their melting temperature. In other words, the proton transfer oc-curs in solid state [4,12–14]. It, however, should be noted that as the proton transfer step depends on not only the hydrogen bond network but also the molecular movement such as reorientation of the heterocycles. The heterocycles in solid state may not effectively experience molecular movement to initiate the significant proton conductivity. This leads us to consider the proton transfer of the heterocycles in the liquid state where the thermal motion is sig-nificant [9]. Currently, several reports applied imidazolides [17,18], triethylamine salts [19], etc. as ionic liquids in Nafion® membrane and showed the proton conductivity in the range of 10^{-3}–10^{-2} S cm^{-1} at 130 °C [17,19,20]. Those studies indicated how the molecules were functioned when they were in the liquid state at room temperature. The stability of ionic liquid in the membranes has to be taken into the consideration [21–23].

It comes to our viewpoint that apart from ionic liquids, the molecular mobility of heterocycles can be more highly enhanced in the molten state. It can be expected that one may be able to control the melting temperature by introducing the alkyl chain segments as a tail of heterocycles and by varying its length. Urocanic acid is convenient since it has an imidazole group with carboxylic acid side chain, which can be combined with variable alkyl chains especially by the esterification. The packing mode and mobility of the side chain is directly related to the melting temperature. In the present work, the urocanic acid and their ester derivatives, i.e. alkyl uro-canates, are used as the model compounds to investigate the roles of both the hydrogen bond network and chain mobility especially in the molten state. The present study consists of the two stages: the structural analysis of the crystal structures to know the molecular shapes and their packing modes in the crystal lattice, which are important for the clarification of the intermolecular interactions including the hydrogen bonds and alkyl chains. The second is to correlate the structure information with proton transfer efficiency. That is to say, these alkyl urocanates were blended with SPEEK and the conductivity was measured as a function of alkyl chain length, leading us to know the role of alkyl chain segment in the enhancement of proton conductivity in the membrane.

2. Experimental

2.1. Materials

Urocanic acid and deuterated-dimethylsulfoxide (DMSO-d_6) were purchased from Aldrich, Germany. Sodium hydroxide, meth-anol, and ethanol were obtained from Carlo Erba, Italy. Hydro-chloric acid (HCl) 35%, DMSO and 1-butanol were purchased from Labscan, Ireland. 1-Propanol, 1-pentanol, 1-hexanol, and 1-hepta-nol were bought from Merck, Germany. Glass filter paper, GC-50, was bought from Advantec, Japan. Poly ether ether ketone (PEEK) was the gift from JJ Degussa Chemical (Thailand) Ltd.

2.2. Preparation of alkyl urocanates

Esterification of urocanic acid with variable chain lengths as alkyl urocanates (Scheme 1) was carried out according to the re-ports by D'Auria et al., 1998 [24] and Sergeyeva et al., 2010 [25]. In brief, urocanic acid (1 g, 7.24 mmol) was dissolved in methanol (60 mL) with a catalytic amount of HCl. The solution was refluxed for a day to obtain the yellowish solution. After the insoluble part was filtrated, the clear yellowish solution was evaporated under vacuum at 80 °C to obtain solid particles (0.5 g). The particles were dissolved in deionized (DI) water before adding few drops of po-tassium carbonate solution (5 mol L^{-1}) and stirring in cold water bath until becoming suspension. The precipitates were filtrated and washed several times by cold DI water before drying at room temperature to obtain the yellowish powder, methyl urocanate, **C1U** (43% yield).

Similarly, ethyl urocanate (**C2U**, 45% yield), iso-propyl urocanate (**C3U**, 35% yield), butyl urocanate (**C4U**, 37% yield), pentyl urocanate (**C5U**, 40% yield), hexyl urocanate (**C6U**, 45% yield), and heptyl urocanate (**C7U**, 42% yield) were prepared.
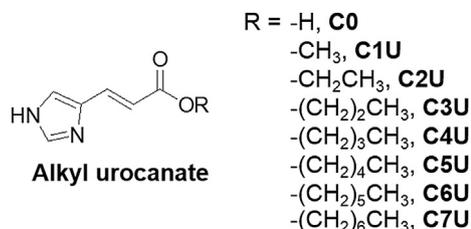
2.3. Characterization

Fourier transform infrared spectra (FTIR) were obtained from a Bruker Equinox 55 FTIR spectrometer with a resolution of 2 cm^{-1}. Electrospray ionization mass spectra (ESI-MS) were analyzed by using a Micro TOF II, Bruker instrument equipped with Bruker Compass DataAnalysis 4.0 software operating in positive ion mode.

^{1}H nuclear magnetic resonance (NMR) spectra were obtained from a Bruker Avance 500 MHz NMR spectrometer using DMSO-d_6 as the solvent. T_1-relaxation time was observed by using ^{1}H NMR evaluated from inversion recovery ($\pi-\tau-\pi/2$) measurements.

Thermal analyses were performed by using a Perkin Elmer Pyris Diamond thermogravimetric analyzer at a heating rate of 10 K min^{-1} under nitrogen atmosphere from 30 °C to 850 °C, and also by a Netzch 200 F3 Maia differential scanning calorimeter at a heating rate of 2 K min^{-1} and a cooling rate of 2 K min^{-1} under nitrogen atmosphere from −90 °C to 150 °C. In the case of **C0**, the analysis was done from −90 °C to 230 °C.

Single crystals were prepared by re-crystallizing the compounds in acetonitrile and chloroform. The structural analysis was done by

R = -H, **C0**
-CH$_3$, **C1U**
-CH$_2$CH$_3$, **C2U**
-(CH$_2$)$_2$CH$_3$, **C3U**
-(CH$_2$)$_3$CH$_3$, **C4U**
-(CH$_2$)$_4$CH$_3$, **C5U**
-(CH$_2$)$_5$CH$_3$, **C6U**
-(CH$_2$)$_6$CH$_3$, **C7U**

Alkyl urocanate

Scheme 1.