

# Brønsted Acid-Base Ionic Liquids as Fuel Cell Electrolytes and Factors Governing Their Proton Conduction under Nonhumidifying Conditions

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## INTRODUCTION

Ionic liquids, also known as room temperature molten salts, are receiving an upsurge of interest in multidisciplinary areas due to, *inter alia*, their immeasurably low vapor pressure, high ionic conductivity, and greater thermal and electrochemical stability. Possessing the wealth of desirable electrochemical and materials properties, these ubiquitous materials also appear to be very promising as electrolytes for polymer electrolyte fuel cells (PEFC), which are at present, associated with a number of constraints originating from the use of easily evaporating water. For their true use as proton conductors, ionic liquids need to act as proton solvents or themselves be capable of proton conduction.

Recently, we have shown that Brønsted acid-base systems, constituting a very important subgroup of ionic liquids, are proton conducting and can serve as fuel cell electrolytes under nonhumidifying and elevated temperature conditions [1-3]. To realize solid-state anhydrous proton conductors, the unique characteristics of the ionic liquids need to be retained while ensuring fast proton conduction in the solid-states, which necessitates proper choice of the acid-base systems and optimization of the factors governing proton transport. This study aims at providing a deep insight into the proton conduction behavior of a wide variety of acid-base ionic liquids, with special emphasis on the development of criteria for the design of solid-state fast proton conductors.

## EXPERIMENTAL

Appropriate amounts of bis(trifluoromethane sulfonyl)imide (HTFSI) and a wide variety of organic amines, maintaining defined molar ratios were mixed and heated above the respective melting points in an argon atmosphere glove box to have a novel series of protic ionic liquids. The thermal properties were studied using thermogravimetry (TG) and differential scanning calorimetry (DSC), while ionic conductivities were determined by complex impedance methods. The <sup>1</sup>H-NMR spectra of the ionic liquids were taken by using a double tube. Self-diffusion coefficients were determined by pulsed-gradient spin-echo (PGSE) NMR measurements. The electrochemical activity and proton transport behavior of the ionic liquids were analyzed at the three-phase boundary of the ionic liquids/Pt/N<sub>2</sub>, H<sub>2</sub> or O<sub>2</sub> by electrochemical polarization experiments.

## RESULTS AND DISCUSSIONS

Most of the amines formed neutral salts, which showed high thermal stability as an ionic liquid, for instance, the comment of decomposition for the salt of 4,4'-trimethylene dipiperidine with HTFSI could be observed at temperatures >400 °C. Notably, the neutral salts of 1,2,4-triazole, triethylamine, and butylamine with

HTFSI are liquid at room temperature. The melting point ( $T_m$ ) of the systems changes with change in compositions. The neutral salt for imidazole (Im)/HTFSI melts at 73 °C and the  $T_m$ s of other compositions are lower than those of the equimolar salt and Im or HTFSI, giving eutectics between the equimolar salt and Im or HTFSI. Some compositions with certain molar ratios of Im and HTFSI are liquid at ambient temperature.

The equimolar salts exhibited high conductivity ( $\geq 10^{-2} \text{ Scm}^{-1}$ ) with notable differences in ionic conductivity ( $\sigma$ ) for the variation in the constituting amines. The  $\sigma$  has also been found to depend strongly on temperature and composition of the systems. For the Im/HTFSI system, the  $\sigma$  increases with increasing Im mole fraction with a sharp decrease for neat Im. Interestingly, the  $\sigma$  for [Im]/[HTFSI] = 9/1 attains the value of ca.  $0.1 \text{ Scm}^{-1}$  at 130 °C.

The analyses of the conductivity, <sup>1</sup>H NMR chemical shift, self-diffusion coefficient, and electrochemical polarization results indicate that the neutral salts as well as the base-rich compositions are proton conducting and that proton conduction in the representative amine-HTFSI systems depends on the composition. Some of the systems studied are electroactive for H<sub>2</sub> oxidation and O<sub>2</sub> reduction at a Pt electrode under nonhumidifying conditions and provide clear evidences for electric power generation by a H<sub>2</sub>/O<sub>2</sub> fuel cell at elevated temperatures.

The self-diffusion coefficients, in association with the ionic conductivity data, provided valuable information on the extent of structure diffusion (Grotthuss mechanism) and matrix transport (vehicle mechanism) of the ionic liquid systems of our interest, and the proton transference number and Grotthuss contribution of proton transport could also be estimated. These enabled the correlation of the factors such as, the difference of the acid dissociation constants of the acid and base ( $\Delta \text{p}K_a$ ), symmetry, molecular structure, orientation in space, local mobility, and composition of the component amines, and temperature of the systems with proton conduction for a wide variety of acid-base ionic liquids. The impact of the factors governing proton transport will be discussed for the construction of solid-state proton anhydrous conductors based on the concept of ionic liquids or an acidic site and/or a basic site affixed to a polymer backbone.

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