Synthesis and Electrical Characterization of Protonic Ionic Liquid Type Polymers for Application to PEFC Electrolytes

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Abstract

Water is essential for proton conduction in Nafion® which is used in polymer electrolyte fuel cells (PEFCs), so its power generation performance is degraded at high temperatures above 100°C. We are therefore promoting the development of ionic liquid type polymers that have proton conductivity. By using proton-conducting ionic liquid type polymers as electrolyte membranes, we aim to achieve water independent power generation in the high temperature range above 100°C. In this study, polymer electrolyte was synthesized from ionic liquid monomers bearing polymerization functional group. As electrical properties, the ion conductivity behavior of the electrolyte membranes was evaluated by AC and DC methods.

1. Introduction

Polymer electrolyte fuel cells (PEFCs) can continuously generate power through an electrochemical reaction of oxygen and water. In addition, PEFCs are attract much attention to as a clean energy source because they emit only water. PEFCs have various advantages such as small size, light weight, and no liquid leakage due to the use of polymer membranes as the electrolyte, and its practical use as power sources automobiles and household is accelerating. Nafion® is generally used as the electrolyte membrane in PEFCs, but because water is essential for proton conduction its power generation performance decreases at temperatures above 100°C. In this study, we focused on ionic liquid type polymers as polymer membranes that can conduct protons independent of water. They are many unique properties that differ from conventional liquids, such as high polarity, difficult to volatilize, and high ion conductivity. We synthesized ionic liquid type polymers by using protonic ionic liquids as monomers. These polymer electrolyte membranes can operate at temperature above 100°C because water is unnecessary proton conduction.

2. Experiment

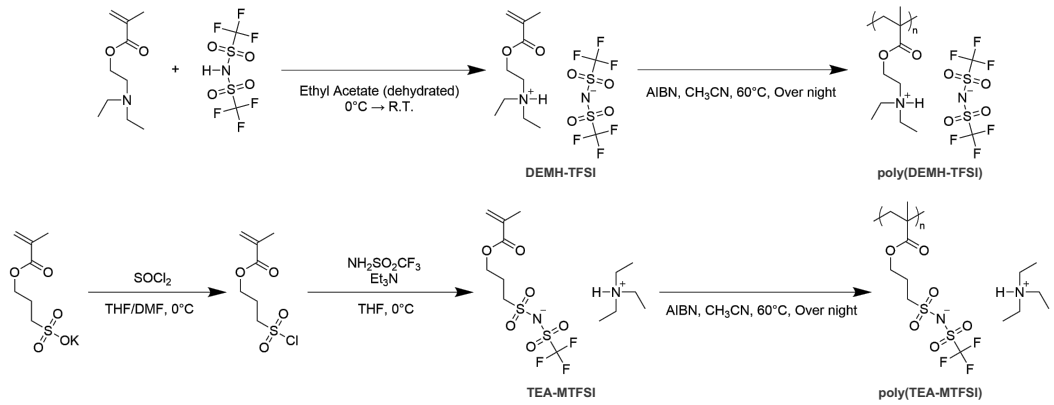
2.1 Synthesis of Ionic Liquid Type Polymers

DEMH-TFSI and TEA-MTFSI were designed, which are monomers with polymerizable functional groups introduced into the cationic part and anionic part, respectively. These monomers were synthesized according to Scheme 1, and then ionic liquid type polymers poly(DEMH-TFSI) and poly(TEA-MTFSI) were synthesized by radical polymerization.

2.2 Electrical Characterization

The ion conductivity is an important parameter in the evaluation of electrolyte membranes, and AC impedance measurement is the mainstream method. It is also important to evaluate

PEFCs by the DC four-terminal (D.C.4) method, because PEFCs are DC devices, to study electrolyte materials for PEFC applications. In the D.C.4 method, we considered it would be possible to directly evaluate the ion conductivity behavior close to the actual power generation situation by measuring the membrane electrode assembly (MEA) under H_2 gas atmosphere. Therefore, the ion conductivity was evaluated by the DC and AC methods in this study.



Scheme 1. Synthesis of poly(DEMH-TFSI) and poly(TEA-MTFSI)

3. Results and Discussion

Temperature dependence of ion conductivity follows the Arrhenius equation, and in this study, Arrhenius plot was used to compare each sample. In AC impedance measurements, the ion conductivity of Nafion® was about 10^{-4} S cm^{-1} to 10^{-5} S cm^{-1}. Those of ionic liquid type polymers indicated about 10^{-3} S cm^{-1} to 10^{-6} S cm^{-1} for poly(DEMH-TFSI) and 10^{-7} S cm^{-1} to 10^{-8} S cm^{-1} for poly(TEA-MTFSI), respectively. Activation energy (E_a) which is calculated from the slope of the Arrhenius plot is important physical property value. E_a is known to have a specific value for each conduction carrier, and E_a for proton conduction is about 30 kJ mol^{-1}. To calculate E_a value from results, Nafion® was approximately E_a = 26 kJ mol^{-1}, poly(DEMH-TFSI) was E_a = 66 kJ mol^{-1}, and poly(TEA-MTFSI) was E_a = 25 kJ mol^{-1}. E_a of Nafion® and poly(TEA-MTFSI) are close result to the literature proton value, it was suggested that conducting carriers are protons. In contrast, E_a of poly(DEMH-TFSI) is different from the literature value of proton conduction, suggesting $TFSI^-$ conduction.

4. Conclusions

Ionic liquid type polymers bearing proton conduction were synthesized and measured conductivity. The ion conductivity measurements showed that all samples followed Arrhenius equation. In the evaluation of activation energy, it was showed that proton conduction may have occurred in Nafion® and poly(TEA-MTFSI), on the other hand, $TFSI^-$ conduction may have occurred in poly(DEMH-TFSI).

Acknowledgments

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