



Preparation of polymer electrolyte membrane with nanomatrix channel through sulfonation of natural rubber grafted with polystyrene

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ARTICLE INFO

Article history:

Received 27 July 2014

Received in revised form 30 September 2014

Accepted 30 September 2014

Available online 17 November 2014

Keywords:

Nanomatrix channel

Graft-copolymerization

Natural rubber

Polymer electrolyte membrane

ABSTRACT

The mechanism of proton transport of a polymer electrolyte membrane (PEM) with nanomatrix channel was investigated with respect to the activation energy of proton conductivity. The PEM with nanomatrix channel was prepared by graft-copolymerization of styrene onto deproteinized natural rubber (DPNR) followed by sulfonation with chlorosulfonic acid. The resulting sulfonated graft-copolymer (SDPNR-*graft*-PS) was characterized by FT-IR spectroscopy, solid-state ¹³C CP/MAS NMR spectroscopy, elemental analysis, transmission electron microscopy (TEM) and impedance analysis. The PEM was found to form completely continuous nanomatrix channel consisting of natural rubber particle of about 1 μm in average diameter as a dispersoid and sulfonated polystyrene of about 60 nm in thickness as a matrix. The value of the activation energy of proton conductivity estimated from the slope of Arrhenius plot was 12 kJ/mol for SDPNR-*graft*-PS, suggesting that the proton transport occurred in a manner of Grotthuss mechanism.

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1. Introduction

The mechanism of proton transport is widely recognized to be indispensable to understand the role of polymer electrolyte membrane (PEM) in fuel cell, which is useful to design a novel PEM as a factor. For instance, the mechanism of the proton transport for perfluorosulfonic acid is classified into two categories, that is, Grotthuss mechanism and vehicle mechanism, in which the protons are transported by connecting ion cluster of 20 to 30 nm in diameter through a channel of several nm in thickness [1]. The difference in the proton transport between the two mechanisms is schematically illustrated in Fig. 1. In the vehicle mechanism, the protons are transported by diffusing into water as hydrated proton aggregates. In the Grotthuss mechanism, in contrast, the protons are transported by jumping from one sulfonic acid to the other through aqueous environment, in which an effective proton concentration may be an important factor for the proton transport. It is therefore quite important to investigate the relationship between proton conductivity and temperature since the effective proton concentration of PEM may be estimated from Arrhenius plot.

In our previous works [2,3], nanomatrix channel was proposed to be the novel nano-phase separated structure for the effective proton transport, which consisted of particles of hydrophobic polymer of about 1 μm in diameter covered with a nano-layers of hydrophilic polymer. It possessed infinite paths of nano-channel to transport the protons, which

was useful for the PEM. The nanomatrix channel was formed by graft-copolymerization of styrene onto surface of natural rubber particles in latex stage followed by sulfonation with chlorosulfonic acid, as shown in Fig. 2. A proton conductivity of the resulting PEM (SDPNR-*graft*-PS) was higher than that of sulfonated polystyrene and perfluorosulfonic acid membranes. However, we have not investigated the mechanism of the proton transport of SDPNR-*graft*-PS.

Many studies on the proton transport of the PEM have been performed with sulfonic acid containing membranes [4–8]. Yeo [9] reported that the proton conductivity of the PEM increased with increasing temperature, and it was dependent upon water content on the basis of the ion cluster model. Moreover, Zhong and co-workers [10] estimated an activation energy of the PEM to investigate a mechanism of the proton transport: that is, 14–40 kJ/mol for Grotthuss mechanism and more than 40 kJ/mol for vehicle mechanism. Therefore, it is possible to investigate the mechanism of the proton transport of PEM with nanomatrix channel with respect to the activation energy of the proton conductivity.

In the present study, condition of graft-copolymerization of styrene onto deproteinized natural rubber (DPNR) in latex stage was optimized to prepare DPNR-*graft*-PS. The resulting DPNR-*graft*-PS was sulfonated with chlorosulfonic acid to prepare a PEM with nanomatrix channel. The resulting sulfonated graft-copolymer (SDPNR-*graft*-PS) was characterized by FT-IR spectroscopy, solid-state ¹³C CP/MAS NMR spectroscopy, elemental analysis, transmission electron microscopy (TEM) and impedance analyzer. The proton conductivity was analyzed as a function of temperature.

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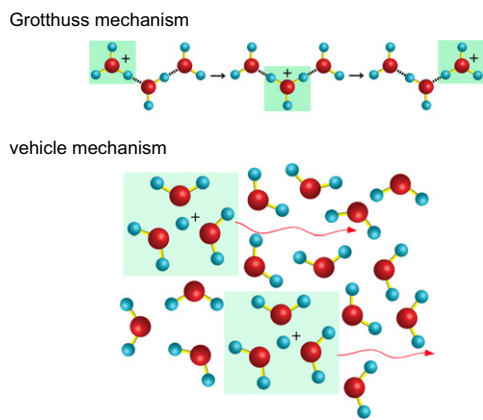


Fig. 1. Schematic illustration of proton transport in PEM.

2. Experimental

2.1. Materials

Natural rubber latex used in the present study was commercial high-ammonia natural rubber (HA-NR) latex (Golden Hope, Malaysia) of about 60% dry rubber content (DRC). Sodium dodecyl sulfate (SDS: 98%), *tert*-butylhydroperoxide (TBHP) and tetraethylenepentamine (TEPA) were purchased from Kishida Chemical Co., Ltd. Chloroform-*d* (99.8%), chloroform (99%) and chlorosulfonic acid (97%) were purchased from Wako Pure Chemical Industry Ltd. Styrene monomer (99%) was purchased from Tokyo Chemical Industry Co., Ltd. Methanol (99.5%), toluene (99.5%), sodium hydroxide (NaOH: 97%) and urea (99.5%) were purchased from Nacalai tesque Inc. Ruthenium tetroxide (RuO_4) was prepared by oxidation of ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot \text{H}_2\text{O}$) with sodium hypochlorite solution (NaClO) purchased from Aldrich and Nacalai tesque Inc., respectively.

2.2. Preparation of DPNR

Deproteinization of natural rubber was performed by incubation of natural rubber latex with 0.1 wt% urea in the presence of 1 wt% SDS at room temperature for 1 h followed by centrifugation at 10^4 rpm. The

cream fraction after centrifugation was re-dispersed in 0.5 wt% SDS solution to make 30 wt% DRC latex, and it was washed twice by centrifugation to prepare DPNR latex. The DRC of DPNR latex was adjusted to 30 wt% with distilled water and SDS was added up to 0.1 wt %.

2.3. Preparation of DPNR-graft-PS

Graft-copolymerization of DPNR latex was carried out with styrene as a monomer, using TBHP/ TEPA as an initiator. DPNR latex was charged with N_2 gas for an hour at 30°C . 3.3×10^{-2} mol/kg-rubber of initiator and 1.5 mol/kg-rubber of monomer were added in turn to the latex, respectively. The reaction was carried out by stirring the latex at about 400 rpm for 5 h at 30°C . The un-reacted styrene was removed by using a rotary evaporator under reduced pressure. The as-cast film of the DPNR-graft-PS was prepared by casting the gross polymer latex into a Petri-dish, and it was dried under reduced pressure at ambient temperature for more than a week. The gross polymer was extracted with acetone/2-butanone 3:1 mixture in a Soxhlet apparatus under nitrogen atmosphere in the dark and dried under reduced pressure for a week, in which the removal of almost all free-polystyrene, isolated from natural rubber, was completed by the extraction for 24 h.

2.4. Preparation of SDPNR-graft-PS

Sulfonation of DPNR-graft-PS was performed by the following procedure. The DPNR-graft-PS film was immersed in chloroform for 5 min until swollen. The sulfonation of the DPNR-graft-PS was carried out with a solution of 0.8 N chlorosulfonic acid in chloroform at 30°C for 5 h. After completion of the sulfonation, the resulting membrane was immersed into methanol for 30 min, followed by washed several times with ion-exchange water until water was neutral. The resulting SDPNR-graft-PS was dried under reduced pressure at 50°C . Prior to characterizations of the SDPNR-graft-PS, the membranes were acidified with 0.5 mol/L H_2SO_4 solution at 80°C for 1 h and rinsed with water. Then, they were boiled with ion exchange water at 80°C for 1 h, twice, followed by dried under reduced pressure at 50°C for a week.

2.5. Characterization

NMR measurements were carried out using a JEOL ECA-400 spectrometer operating at 399.65 and 100.4 MHz for ^1H and ^{13}C , respectively. For a solution state ^1H NMR measurement, the rubber was dissolved into

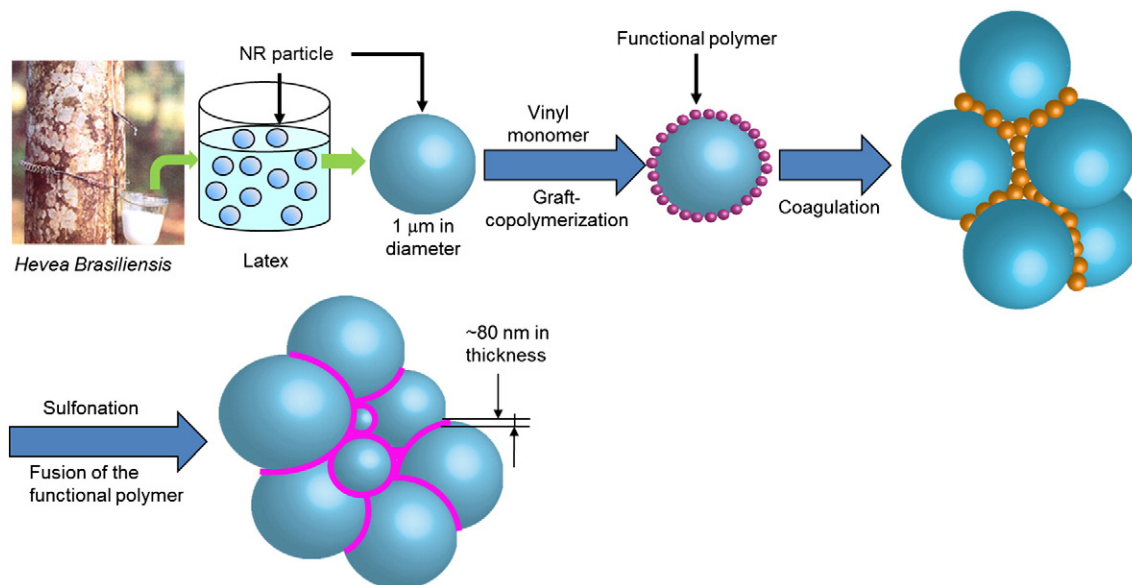


Fig. 2. Preparation of PEM with nanomatrix channel from natural rubber.

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