



A novel environment-friendly route to prepare proton exchange membranes for direct methanol fuel cells

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ABSTRACT

For the past decade, much effort has been dedicated to non-fluorinated polymeric membranes as alternatives for commercial Nafion in the field of direct methanol fuel cells (DMFCs). However, most of researches have used solvents that are environmentally unfriendly during the membranes preparation. This work reported a novel solvent-free route to prepare non-fluorinated proton exchange membranes (PEMs) via the in situ reaction and grafting of sodium 4-styrene sulfonate (NaSS) to hydrogenated nitrile butadiene rubber (HNBR) during peroxide curing. Membrane morphology was characterized by TEM and SEM-EDX experiments. The effect of NaSS loading and unsaturation level of HNBR on the membrane properties were studied. The obtained membranes exhibited proton conductivity on the order of 0.01 S/cm and selectivity (the ratio of proton conductivity to methanol permeability) higher than that of Nafion, and could be potentially used for the application in DMFCs.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted great interest in both academic and industrial field due to their potentials for wide range of applications, especially in the area of portable power generation. As the key component in DMFCs, the proton exchange membranes (PEMs) need to meet the following requirement: high proton conductivity, low methanol permeability, high chemical and mechanical stability and low cost [1–4]. Current state-of-the-art PEM, Nafion, is widely used in hydrogen PEM fuel cells. However, Nafion does not work well in DMFCs because it has too high methanol permeability and it is expensive. Another issue with Nafion is the environmental and health problem caused by fluorine-containing compounds released when Nafion is decomposed. Therefore, low cost and high-performance sulfonated hydrocarbon PEMs have become one of the main research topics during the past few years [3,5–7].

In general, sulfonated hydrocarbon PEMs, including sulfonated polystyrene and its derivatives, sulfonated polyarylene-type polymers, sulfonated polyimides, sulfonated polyphenylenes, and sulfonated polyphosphazenes, can be prepared based on any or combination of the following methods: post-polymerizations sulfonation, direct copolymerization of sulfonated monomers and physico-chemical modification of the sulfonated polymers [2,3,7–17]. As one of the simplest vinylic moieties containing sulfonated functional groups, styrene sulfonate has been investigated extensively to be included in PEMs for DMFCs. Prakash et al. [18] prepared the poly(styrene sulfonic acid)/poly(vinylidene fluoride) (PSSA/PVDF) based PEMs with semi-interpenetrating polymer network (sIPN) structure via the post-polymerization sulfonation method: styrene and divinylbenzene were first polymerized in PVDF matrix to form crosslinked polystyrene/PVDF sIPN composite, and then the composite was sulfonated by chlorosulfonic acid. The prepared membranes achieved comparable proton conductivity as Nafion but with much lower methanol permeability. Shen et al. [19] used the radiation method to graft styrene monomer onto PVDF film and then ran the post-polymerization sulfonation to obtain the PEMs with superior DMFC performance than Nafion membrane. Su et al. [20] reported direct grafting of sodium 4-styrene sulfonate (NaSS) monomer onto electron beam irradiated PVDF to prepare PEMs, but the selectivity was not as good as Nafion. Kim et al. [21] fabricated the crosslinked poly(vinyl alcohol) (PVA) based PEMs

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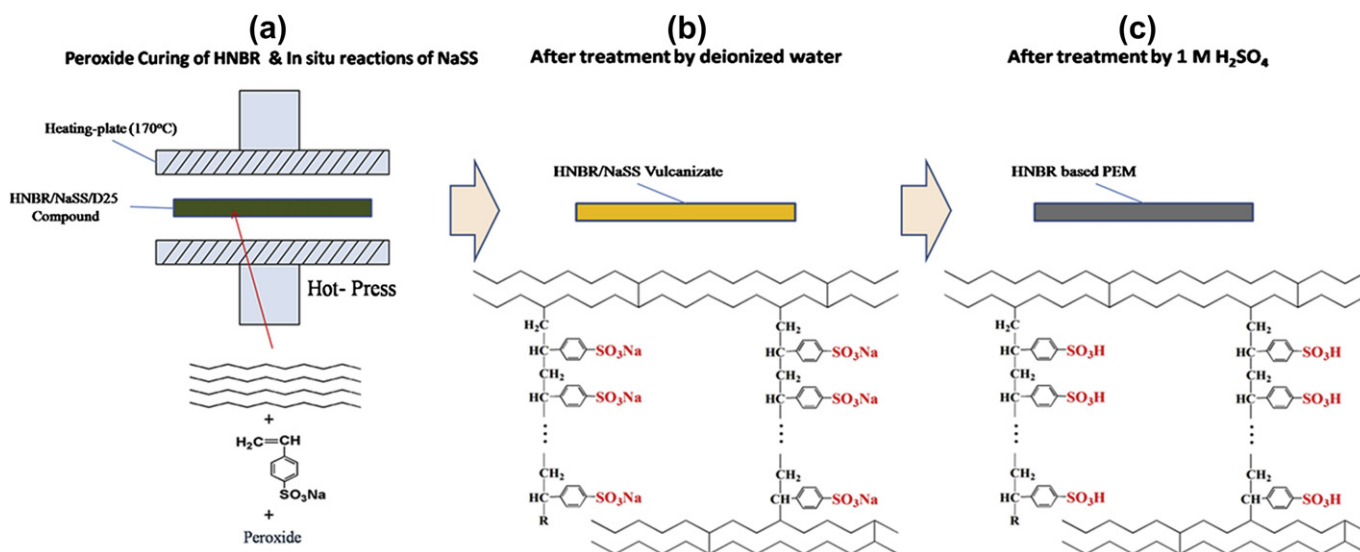


Fig. 1. Schematic of the preparation procedure of the HNBR based PEMs.

with poly(styrene sulfonic acid-co-maleic acid) (PSSA-MA) acting as both cross-linking agent and proton conductor. Both proton conductivity and methanol permeability for the best membrane obtained were one order of magnitude lower than Nafion. Yang et al. [22,23] used nano-sized inorganic fillers (TiO₂ or MMT) to modify PVA/PSSA based materials to form proton-conducting composite membranes with low methanol permeability and obtained better DMFC performance than Nafion. In addition to their study, most of the research work on PEMs reported in the literature however applies significant amount of solvent during the synthesis and membrane preparation process, which will cause serious environmental and health problem.

Recently, Wu et al. [24] reported synthesis of alkaline anion conductive membranes via a solvent-free strategy, in which the mixture of vinylbenzylchloride (VBC) and divinylbenzene (DVB) monomers first acted as solvent to dissolve brominated poly(2,6-dimethyl-1,4-phenylene oxide) (BPPO) and then underwent in situ polymerization to incorporate BPPO into the network of poly(VBC-DVB). This promising method however requires careful selection of monomers and polymers so that a homogenous solution could be formed.

Solid state grafting technique that involves no solvent has been applied in a wide range of areas, such as rubber reinforcement [25,26], polyolefin modification [27–29] and polymer composite formation [30]. In this work, we described for the first time an all solid-state solvent-free route to prepare PEMs via the in situ reaction and grafting of NaSS to hydrogenated nitrile butadiene rubber (HNBR) matrix during peroxide curing. The membrane structure and morphology were characterized via FTIR and electron microscopy techniques. The effect of unsaturation level of HNBR matrix and the content of NaSS on the properties of the prepared PEMs was examined and discussed.

2. Experiment

2.1. Materials

HNBR2010L (36% acrylonitrile and 4% double bond) and HNBR2020L (36% acrylonitrile and 10% double bond) were purchased from Zeon Co. Ltd., Japan. NaSS was supplied by Yixin

Chemical Co. Ltd., China. The peroxide initiator, 2,5-bis(tert-butylperoxy)-2,5-dimethyl hexane (D25), was purchased from Akzo Nobel Cross-Linking Peroxide Co. Ltd., China.

2.2. Membrane preparation

The formulation of the HNBR/NaSS consisted of 100 phr HNBR, 8 phr D25, and variable amount of NaSS (from 20 up to 110 phr). The samples are designed as HNBR/NaSS (100/x), where x refers to the amount of NaSS (in phr) added in the formation.

An open 6-inch two roll mill was used to blend the HNBR/NaSS (100/x) samples, and the peroxide initiator D25 was added during mixing process. The HNBR/NaSS vulcanizate films were obtained by compression molding using a hot press, in which the peroxide curing of HNBR and in situ reaction of NaSS were carried out during the molding process at 170 °C (D25 has the suitable decomposition rate at this temperature) under the pressure of 15 MPa for 30 min. The 30 min curing time was determined from torque vs. time curve measured by a rotorless curemeter (the torque became nearly unchanged when the curing time reached

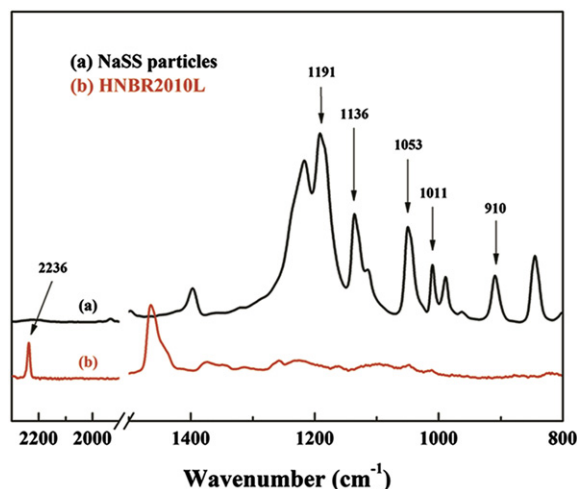


Fig. 2. FTIR spectra of NaSS particles and HNBR2010L.

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