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Proton exchange membranes prepared via atom transfer radical polymerization for proton exchange membrane fuel cell: Recent advances and perspectives

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ABSTRACT

Proton exchange membranes (PEMs) with well-defined microphase separation hold great promise for satisfying the demands of operation under high temperature and low humidity. Atom transfer radical polymerization (ATRP), as one of the most popular methods of controllable polymerization, has already been one of the most convenient tools for the synthesis of copolymers with well-defined microphase separated structures. This article tersely and concisely reviews the recent development of the PEMs prepared by ATRP for proton exchange membrane fuel cells. According to the different functional monomers in the polymerization, three kinds of membranes are systematically discussed in this feature article. The first membrane is made of copolymer grafted styrene by ATRP followed by post-sulfonation; the second membrane is prepared by directly grafting a sulfonated monomer to polymer using single-step ATRP; and the membranes grafted other types of monomers are divided into the third membranes. For each category of membrane, structures, properties, and their relationships are conducted targeted analysis. Finally, the perspectives of future trends on PEMs prepared via ATRP are presented.

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Introduction

Proton exchange membrane (PEM), an essential component of proton exchange membrane fuel cell (PEMFC), is used not only as a proton conductor but also as a separator for separating the hydrogen fuel from the oxidant in the PEMFC [1,2].

Currently, perfluorosulfonic acid membranes such as Nafion, are the most commonly used as PEMs because of their excellent electrochemical property, chemical stability and outstanding proton conductivity [3–5]. However, to our knowledge, several perceived problems of Nafion membranes including high cost, high fuel permeability and restricted properties under the more stringent operating conditions (at

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Nomenclature

ATRP	Atom transfer radical polymerization
PEM	Proton exchange membrane
PEMFCs	Proton exchange membrane fuel cells
RH	Relative humidity
SPS	Sulfonated polystyrene
PVDF	Poly(vinylidene fluoride)
VBC	Vinylbenzyl chloride
CTFE	Chlorotrifluoroethylene
IEC	Ion exchange capacity
DS	Degree of sulfonation
PVC	Polyvinyl chloride
PP	Poly(bis(4-methylphenoxy) phosphazene)
ETFE	Ethylene-co-tetrafluoroethylene
BrTFF	2-bromotetrafluoroethyl trifluorovinyl ether
HEMA	Hydroxyl ethyl methacrylate
SPS	Sulfonated polystyrene
SA	Sulfosuccinic acid
SI-ATRP	Surface initiated atom transfer radical polymerization
POSS	Polyhedral oligomeric silsesquioxane
HPSS	Hollow polymer microspheres grafted with sulfonated polystyrene brushes
PFSA	Perfluorosulfonic acid
SPEEK	Sulfonated poly(ether ether ketone)
SSNa	Sodium styrene sulfonate
MEA	Membrane electrode assembly
SSA	Styrene sulfonic acid
HEA	Hydroxyethyl acrylate
HEMA	Hydroxyl ethyl methacrylate
TMSPMA	3-(trimethoxysilyl) propyl methacrylate
PVA	Poly(vinyl alcohol)
PVDF-HFP-g-PSSA	Poly(vinylidene fluoride-co-hexafluoropropylene) grafted poly(styrene sulfonic acid)
SPMA	3-sulfopropylmethacrylate
PESEKK-g-PSPMA	Poly(ether sulfone ether ketone ketone) grafted poly(sulfopropyl methacrylate)
PSS-g-SiO ₂	Silica particles grafted with sodium4-styrenesulfonate
SHNT	Sulfonated halloysite nanotubes
IDA	Imidazole dicarboxylic acid
H ₃ PO ₄	Phosphoric acid
PGMA	Poly(glycidyl methacrylate)

temperatures above 80 °C and relative humidity (RH) conditions below 50%), have been gradually emerging in the developing process [6,7]. Accordingly, extensive efforts have been devoted to developing alternative and low-cost materials to prepare the state-of-the-art membranes with greatly improved performance at elevated temperatures and reduced RH [8–10]. For decades, this approach concentrated primarily on the development of polymers, including partially fluorinated acidic ionomer membranes [11,12], sulfonated poly(arylene ether)-based membranes [13,14], sulfonated polyimide-based membranes [15,16] and different variants of composite membranes [17–19]. On the basis of all these

researches, a promising way is inducing microphase separated morphology between the hydrophilic and hydrophobic matrix to construct proton transport channels and optimize water regulation [20]. For one thing, an ordered hydrophilic morphology will influence the proximity of acid groups within the polymer architecture and the degree of tortuosity of proton conduction pathway, which could improve the ion mobility; for another, an ordered hydrophobic morphology will provide a structural framework for tuning fuel permeability, thermal stability, and mechanical stability [21–23]. Some of the related work was carried out by the group of Peckha and Holdcroft [24]. They confirmed that the formation of a microphase-separated morphology composed of ion nanochannels and a hydrophobic phase was the most important strategy to simultaneously improve the ion mobility and ion concentration, which could determine the ionic conductivity (ionic conductivity \cong ion mobility \times ion concentration). Guiver's team [25,26] also revealed the structure-morphology-property relationships of non-perfluorinated proton-conducting membranes.

It was known that the preparation of block copolymer [27,28] or graft copolymer [29,30] was a promising way to enhance microphase separation as a result of the enthalpy associated with the demixing of incompatible segment. Li et al. [31–33] have synthesized several block and graft (comb-shaped) copolymers consisting of the highly sulfonated segment and the fully aromatic main chains. These novel copolymers exhibited organized microphase separated morphology with well-connected nanochannels, resulting in a dramatic enhancement in proton conductivity under partially hydrated conditions compared to other hydrocarbon-based PEMs. Wang et al. [34] prepared the highly sulfonated poly(ether sulfone)s with densely populated flexible acid chains, which exhibited clear hydrophilic/hydrophobic phase separation with 5–15 nm width of the hydrophilic domains. Thereby, all the membranes exhibited higher proton conductivity than that of Nafion 212 at 80 °C and 95% RH and their proton conductivities were higher than 10 mS/cm at 50% RH.

Consequently, how to simply and effectively prepare these copolymers for PEMs has been a crucial research topic recently. The reported techniques included ring-opening metathesis polymerization (ROMP) [8], in situ emulsion polymerization (IEP) [35], atom transfer radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT) [36] and other polymerization [37,38]. Among these, ATRP, as one of the most popular methods of controllable polymerization, has already been one of the most convenient tool for the synthesis of block and graft copolymers based on a wide variety of monomers. The mechanism of copper-mediated ATRP used macroinitiator for graft and block copolymers was shown in Scheme 1. Obviously, ATRP involved a reduction-oxidation reaction of a macroinitiator (R-X) and metal halides (CuX). The presence of the ligand improved the solubility of metal salt in the organic reaction system. During the initiation stage, the released electron from the redox process initiated the macroinitiator. The active radical would initiate the monomer and the monomer would propagate becoming an active polymer. Then, polymer will be terminated and end capped by a halide group in the termination stage [39,40]. ATRP could be used to prepare high molecular

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