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Preparation of new self-humidifying composite membrane by incorporating graphene and phosphotungstic acid into sulfonated poly(ether ether ketone) film

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ARTICLE INFO

Article history:

Received 21 May 2014

Received in revised form

25 July 2014

Accepted 30 July 2014

Available online 10 September 2014

Keywords:

Proton exchange membrane

Graphene

Phosphotungstic acid

Self-humidification

Direct methanol fuel cell

ABSTRACT

In this work, a combination of constituent materials capable of improving the moisture retention and proton conductivity (PC) was incorporated into sulfonated poly(ether ether ketone) (SPEEK) membranes in order to prepare new, self-humidifying composite membranes (SHMs) for proton exchange membrane fuel cells. The property-improving components were incorporated into the cast SPEEK film in an appropriate microstructural architecture to prepare the SHMs with increased water retention and PC. SHMs were therefore prepared with the inclusion of carboxyl-functionalized graphene (G(c)) and phosphotungstic acid (PWA) with varying proportions into the SPEEK film. The structure of the SPEEK/G(c)/PWA composite membranes was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, energy dispersive X-ray analysis, thermogravimetric analysis and X-ray photoelectron spectroscopy. The physicochemical properties of the composite membranes, such as ion exchange capacity, water uptake, thermal stability and PC, were investigated. This work provides confirmation that self-humidifying properties are improved at temperature above 60 °C through a combinational inclusion of G(c) and PWA within SPEEK and the new self-humidifying membranes have potential for use in medium temperature direct methanol fuel cells.

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<http://dx.doi.org/10.1016/j.ijhydene.2014.07.181>

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Introduction

During the last few decades, proton exchange membrane fuel cells (PEMFCs) have attracted attention as a potential power source for electric vehicles and residences due to their advantages of high energy density, simplicity of operation, high-energy conversion efficiency and low harmful emissions [1]. One of the important components in PEMFCs is the proton exchange membrane (PEM), which contributes to its function of providing ionic pathways to transfer protons, as well as acting as a separator between the electrodes [2,3]. Nafion[®], the most common, commercially used PEM material, possesses a suitable combination of high proton conductivity (PC) and excellent chemical stability at moderate temperature (<90°C). However, its high cost, high methanol permeability and low conductivity at low humidity or high temperature have limited its commercial applications and have stimulated researchers to investigate promising alternative membranes [4–6]. The operating conditions and water content of the PEM influences the proton conductivity in an extremely complicated way [7,8]. Water management is therefore a critical issue in the operation of a fuel cell.

Many investigations are presently focusing on sulfonated poly(ether ether ketone) (SPEEK) as a substitute for perfluorosulfonated ionomer-based PEM. Both Nafion[®] and SPEEK membranes require water to maintain PC. Thus, to prevent drying out of the membrane and keep the membrane in its most conductive state, the reactant gases are usually humidified through an external humidification system before entering the fuel cells. However, this method increases the weight and complexity of the fuel cell system, thereby rendering PEMFCs unsuitable for portable applications. The unsaturated-humidification or non-humidification of reactant gases prior to entry into a fuel cell may decrease the water content and thus reduce the PC of the membranes [9,10]. The reduction in membrane thickness has facilitated water back diffusion from the cathode to the anode. However, this has also accelerated the reactant crossover because of the membrane thinness, which may reduce the cell performance and accelerate the membrane degradation [11]. To suppress the mutual permeation of the reactant gases and attain dry-condition fuel cell operation, most literature has focused on the development of self-humidifying PEMs. The inclusion of external humidifying subsystem introduces complexity, weight and cost to the operation of PEMFCs. It is therefore beneficial to be able to operate PEMFCs without external humidification systems. Research efforts have addressed removing the externally humidifying unit from the PEMFCs by endowing the membrane electrode assembly with self-humidifying ability [12–15]. Watanabe et al. [13,14] proposed the concept of self-humidifying composite membranes and confirmed that the fuels, H₂ and O₂, diffused into the Nafion[®] membrane could be recombined by catalysis with the Pt nanoparticles added in the membrane, thereby decreasing the reactant crossover through the membrane and increasing the water content.

Two approaches, (i) the development of cross-linked membranes and (ii) the incorporation of inorganic fillers, were considered the most effective ways to realize PEM-based

fuel cells that operate without external humidification [16–19]. Crosslinking is thought to be an effective method to restrain water uptake, swelling ratio and methanol crossover. The introduction of the inorganic particles can enhance the mechanical and thermal properties while the organic part can offer specific chemical reactivity and flexibility. Hygroscopic metal oxides such as SiO₂ or TiO₂ were included to adsorb water and improve PC [20,21]. A few proton-conductive particles, such as ZrP and ZrO₂, were included in the PEMs for operating the cell under dry conditions [22,23]. Lee et al. impregnated nanometer-sized Pt crystallites into a Nafion[®] 112 membrane by reduction of Pt (NH₃)₄²⁺, followed by in situ precipitation of zirconium phosphate in the Pt-Nafion[®] membrane. The incorporation of zirconium phosphate in the membrane was expected to improve the cell performance under dry operation due to its high PC and high water-retaining properties [24]. Xing et al. [25] investigated a self-humidifying composite membrane based on SPEEK, which was prepared by first casting SPEEK solution onto porous polytetrafluoroethylene (PTFE) film to obtain SPEEK/PTFE as a base layer and then recasting the ink of SPEEK and Pt/C catalyst onto the SPEEK/PTFE base layer to form a Pt–C/SPEEK layer. Li et al. [26] developed self-humidifying membranes incorporating some proton-conductive particles to improve the proton conductivity of the membrane under dry operating conditions.

Hetero polyacids (HPAs) are a very attractive as inorganic fillers for composite membrane preparation because they are highly conductive and thermally stable in their crystalline form. These acids exist in several hydrated forms depending on the hydration environment [27–29]. HPAs, are super ionic conductors in their fully hydrated state due to three-dimensional conductivity network. Keggin structures of HPA have been effectively used to enhance the PC, water retention and resistance to methanol crossover properties of Nafion[®] and other PEMs. In the hydrated phase, the HPA molecules are bridged by water molecules to form hydronium ions. Haugen et al. and Krawiec et al. suggested that HPA acts as a Brønsted acid toward the water of hydration, which bounds loosely to its structure, resulting in high PC [29,30]. Several researchers reported that the addition of HPAs to perfluorosulfonic acid ionomers improves its PC and durability and improves the performance of membrane electrode assemblies [31–33]. Phosphotungstic acid (PWA), one of the HPAs in the Keggin series has also been used to improve the conductivity and thermal stability of polymer electrolyte membranes [34]. Cesium phosphotungstate salt (Csx-PWA, 0 ≤ x ≤ 3), which contains the characteristic structure of PWA has excellent conductive capability and increased stability in aqueous media. It has been shown that the addition of Csx-PWA enhances the PC and reduced methanol permeability of host matrix materials including SPEEK [35].

In recent years, graphene, has received considerable attention because of its unique properties, including high thermal conductivity (~5000 W m⁻¹ K⁻¹), high electrical conductivity (10⁸ S m⁻¹), high transparency (absorbance of 2.3%), great mechanical strength (breaking strength of 42 N m⁻¹ and Young's modulus of 1.0 TPa), inherent flexibility, high aspect ratio, and large specific surface area (2.63 × 10⁶ m² kg⁻¹) [36,37]. Graphene consists of a single layer of graphite with perfect 2D crystals of sp² hybridized carbon atoms. In

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