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Mixed matrix proton exchange membranes for fuel cells: State of the art and perspectives

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ABSTRACT

Proton-conducting mixed matrix membranes (PC-MMMs) have received considerable interest as promising materials that combine the properties of, and create synergism from interactions between, polymeric and inorganic components. The PC-MMM exhibit superior characteristics compared to individual ion-conducting polymeric membranes or free-standing electrolyte inorganic films. Recent advancements in material preparation have enhanced the ability to design PC-MMMs with specified properties. This critical review discusses the progress of the development of PC-MMMs, with special focus on PC-MMMs based on emerging materials, such as porous materials, metal organic frameworks (MOFs), carbon nanotubes (CNTs) and graphene oxides (GOs). Major challenges facing PC-MMMs and strategies taken to overcome those challenges and future perspectives are discussed.

Contents

Abbreviations: AFC, alkaline fuel cell; AEMFC, anion exchange membrane fuel cell; Al-MSU-F, aluminosilicate mesostructured with cellular foam framework; CMC, critical micelle concentration; CNT, carbon nanotubes; DMFC, direct methanol fuel cell; F–GO, functionalized graphene oxide; GDL, gas diffusion layer; GO, graphene oxide; HPA, heteropolyacids; HRTEM, high resolution transmission electron microscope; IEC, ion-exchange capacity; ICPTES, (3-isocyanatopropyl) trimethoxysilane; MCFCs, molten carbonate fuel cells; MEA, membrane electrode assembly; MMT, montmorillonite; MPs, metal phosphates; MPTMS, mercaptopropyltrimethoxysilane; MWCNT, multi-walled carbon nanotubes; PEM, polymer electrolyte membrane/proton exchange membrane; MOF, metal organic framework; NAF, Nafion®; NAFB, Nafion®/acid functionalized zeolite Beta; PBI, polybenzimidazoles; PC-MMM, proton conducting mixed matrix membranes; PC-MOF, proton conducting metal organic framework; PEMFC, proton exchange membrane fuel cell; PFSA, perfluoro sulfonic acid; SAP, sulfonated aromatic polymer; SEM, scanning electron microscopy; s-MWCNT, sulfonated multi-walled carbon nanotubes; SiWA, silicotungstic acid; SPAES, sulfonated poly(arylene ether sulfone); SPEEK, sulfonated poly(arylene ether ketone); SPES, sulfonated poly(ether sulfone); SPI, sulfonated polyimide; SPPO, sulfonated poly(phenylene oxide); sPS, sulfonated polysulfone; SPS, sulfonated polystyrene; SOFC, solid oxide cells; s-SWCNT, sulfonated single-walled carbon nanotube; SWCNT, single-walled carbon nanotubes; TEOS, tetraethoxysilane; UANs, urethane acrylate non-ionomers; ZrP, zirconium hydrogen phosphates.

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1. Introduction

The need for clean energy during the current rapid growth of technology and population is made more urgent due to the depletion of fossil fuels and natural gases and to the increased destruction to the environment caused by these fuels sources. The global environmental is in danger, and quick and efficient actions to supplant traditional energy sources would benefit future generations. One promising approach for sustainable energy uses fuel cell technology to convert chemical energy to electricity with high efficiency using an electrochemical device called a "fuel cell". Fuel cell technology stands out, especially in transportation and handheld devices, because of its high efficiency. It provides electricity with zero emissions and high energy conversion and produces water when hydrogen is used as the fuel. Fuel cells are classified based on the type of electrolyte used. Fuel cells that are currently under investigation include polymer electrolyte membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), solid oxide cells (SOFCs), phosphoric acid fuel cells (PAFCs) and molten carbonate fuel cells (MCFCs) [1]. When methanol gas is used as the fuel, the PEMFC is termed as a direct methanol fuel cell (DMFC). The ion exchange membrane is crucial for proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs) because it allows for the transport of protons in PEMFCs and hydroxyl ions in AEMFCs while blocking the passage of electrons and fuels.

Fuel cells' versatile applications extend from handheld devices to transportation to large stationary equipment [2]. The global fuel cell market is expanding rapidly, and several automobile makers have started to commercialize green cars at affordable prices aimed at the middle-income population. However, the price of fuel cells is still high. According to the U.S. Department of Energy (DOE), the fuel cell price target is \$40/kW h by 2020. The high cost of PEMFCs is caused mainly by the proton exchange membrane (e.g., Nafion®) and expensive electrode materials (e.g., Pt). However, because PEMFCs use abundant fuel gases (oxygen and hydrogen) and offer the unique advantage of operating at moderate temperatures, substantial effort has been expended to lower the cost and increase the performance of PEMFCs.

Despite extensive modifications made to perfluorosulphonic ionomers (PFSIs), such as Nafion®, Flemion, and Aciplex, the high cost of PFSI membranes is still a serious challenge. Low-cost aromatic polymers have been suggested as a promising alternative for use in PEMFCs. Since the last decade, sulphonated poly(arylene ether)s (SPAES, e.g., SPEEK), sulphonated poly(phenylene oxide) (SPPO), and sulphonated polyimides (SPI) have attracted tremendous attention for potential application in moderate-temperature fuel cells, whereas polybenzimidazoles (PBIs) doped with phosphonic acid or/and heterocycles such imidazole and triazole were investigated as potential candidates for high-operating-temperature and anhydrous PEMFCs [3–7]. Some polymer-based membranes, such as a sulphonated poly(arylene ether sulphone) copolymer membrane, are reported to possess outstanding proton conductivity and good fuel cell performance compared to perfluorosulphonic ionomer membranes [8], but sulphonated aromatic polymer membranes suffer from high swelling, that increases with the increasing degree of sulphonation that is basically responsible for the