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Silicate-based polymer-nanocomposite membranes for polymer electrolyte membrane fuel cells

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ABSTRACT

Proton-exchange membrane fuel cells have emerged as a promising emission free technology to fulfill the existing power requirements of the 21st century. Nafion® is the most widely accepted and commercialized membrane to date and possesses excellent electrochemical properties below 80 °C, under highly humidified conditions. However, a decrease in the proton conductivity of Nafion® above 80 °C and lower humidity along with high membrane cost has prompted the development of new membranes and techniques. Addition of inorganic fillers, especially silicate-based nanomaterials, to the polymer membrane was utilized to partially overcome the aforementioned limitations. This is because of the lower cost, easy availability, high hydrophilicity and higher thermal stability of the inorganic silicates. Addition of silicates to the polymer membrane has also improved the mechanical, thermal and barrier properties, along with water uptake of the composite membranes, resulting in superior performance at higher temperature compared to that of the virgin membrane.

Abbreviations: AIBN, 2,2′-azobis(isobutyronitrile); AMPS, 2-acrylamido-2-methyl-1-propane sulfonic acid; APTES, 3-aminopropyltriethoxysilane; BIS, benzimidazole-sulfonic acid polysiloxane; Boltron, hyperbranched aliphatic Polyester BoltornTM H20; CIM, conventional impregnation method; CTAB, cetyltrimethyl ammonium bromide; DMA, dynamic mechanical analysis; DMAc, dimethyl acetamide; DMDOC, dimethyl dioctadecylammonium chloride; DMF, dimethyl formamide; DMSO, dimethyl sulfoxide; DOE, Department of Energy; DPTS, diethyl phosphonatoethyltriethoxysilane; DS, degree of sulfonation; EB, elongation at break; [EIm][TfO], N-ethylimidazolium trifluoro methanesulfonate; GPTMS, glycidoxy-propyltrimethoxysilane; HCl, hydrochloric acid; HEMA, 2-hydroxyethyl methacrylate; HNO_3, nitric acid; HPMC, hydroxypropyl methyl cellulose; HPW, phosphotungstic acid; HTPEMFC, high temperature polymer electrolyte membrane fuel cell; IPA, isopropyl alcohol; LTPEMFC, low temperature polymer electrolyte membrane fuel cell; MCM, crystalline mesoporous silica; MEA, membrane electrode assembly; MMT, Montmorillonite; MPS, 3-methacryloxypropyl trimethoxysilane; MPTMS, 3-mercaptopropyl-trimethoxysilane; NaOH, sodium hydroxide; NMP, N-methyl-2-pyrrolidone; NMR, nuclear magnetic resonance; P123, Pluronic P123; PA, phosphoric acid; PAA, poly(acrylic acid); PAM, polyamide; PBI, polybenzimidazole; PDMS, polydimethyl siloxane; PEEK, polyether ether ketone; PEG, polyethyleneglycol; PEI, polyether imide; PEM, polymer electrolyte membrane; PEMFC, polymer electrolyte membrane fuel cell; PEO, polyethylene oxide; PFSA, perflurosulfonic acid; phr, parts per hundred; PI, polyimide; PIL, protic ionic liquid; POSS, polyhedral oligomeric silsesquioxane; PPA, polyphosphoric acid; PPO, polyphenyloxide; PS, polystyrene; PSEBS, polystyrene ethylene butylene polystyrene; PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride; PVDF-HFP, poly(vinylidene fluoride-*co*-hexafluoropropylene); PVOH, poly(vinyl alcohol); PWA, tungstophosphoric acid; RH, relative humidity; SA, sulfanilic acid; SAN, poly(styrene-*co*-acrylonitrile); SAXS, small angle X-ray scattering; SBA-15, amorphous mesoporous silica; SDF, sulfonated decafluorobiphenyl; SiO_2-Im, silica containing imidazole group; SiPANPs, silicon-containing polyacrylate nanoparticles; SPAES, sulfonated polyarylene ether sulfone; SPEEK, sulfonated polyether ether ketone; SPOSS, sulfonated polyhedral oligomeric silsesquioxane; SPPO, sulfonated polyphenyloxide; SPSU, sulfonated polysulfone; SPSEBS, sulfonated polystyrene ethylene butylene polystyrene; SPSU-BP, sulfonated poly(biphenyl ether sulfone); STY, styrene; TBS, Zonyl® TBS; TEOS, tetraethylorthosilicate; T_g, glass transition temperature; THF, tetrahydrofurane; TP, poly(vinylidenefluoride-ter-perfluoro(4-methyl-3,6-dioxaoct-7-ene sulfonyl fluoride)-ter-vinyltriethoxysilane); TS, tensile strength; VIM, vacuum-assisted impregnation method.

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However, the degrees of dispersion and interaction between the organic polymer and inorganic silicates play vital roles in improving the key properties of the membranes. Hence, different techniques and solvent media were used to improve the degrees of nanofiller dispersion and the physico-chemical properties of the membranes. This review focuses mainly on the techniques of silicate-based nanocomposite fabrication and the resulting impact on the membrane properties.

Contents

1. Introduction

1.1. Background

Generation of power without the emission of toxic gases is indispensable in the current scenario. The green technologies adopted for power generation include the use of wind and water. However, such technologies are insufficient to fulfill the existing power requirements. Fuel cells have emerged as the most promising field of research in this realm to overcome the energy scarcity owing to their promising clean and efficient energy conversions.

Fuel cells involve the direct conversion of chemical energy into electrical energy through the process of electrochemical oxidation. Fuel cells minimize power loses by avoiding the intermediate steps that are required in similar diesel-powered generators. Schematic depiction of the energy conversion steps involved in a fuel cell and diesel engine are shown in Fig. 1. The first fuel cell was invented by Sir William Robert Grove in 1839 and was based on the electrochemical conversions of hydrogen and oxygen [1–3]. This original development has fostered the creation of several types of fuel cells including proton exchange membrane fuel cells (PEMFC), solid oxide fuel cells, alkaline