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Influence of amine-functionalized iron titanate as filler for improving conductivity and electrochemical properties of SPEEK nanocomposite membranes

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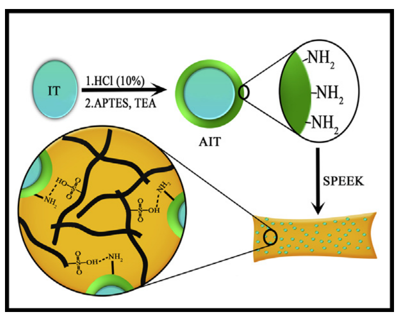
HIGHLIGHTS

- The surface of iron titanate (IT) nanoparticles was modified by grafting APTES.
- Nanocomposites based on amine-functionalized IT and SPEEK were obtained.
- The membranes showed high proton conductivity of 0.12 S cm^{-1} at 80 °C.
- High power density of 201 mW cm^{-2} was obtained in a single PEMFC at 80 °C.
- The prepared membranes are good candidate for PEMFCs.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel proton exchange membrane was easily prepared by incorporating amine-functionalized iron titanate (AIT) nanoparticles into sulfonated poly (ether ether ketone) (SPEEK) polymer matrix. The surface of iron titanate nanoparticles was modified by grafting (3-aminopropyl) triethoxy silane (APTES). AIT nanoparticles were uniformly dispersed within SPEEK membrane due to the good interfacial compatibility. All the membranes were characterized by Fourier transform infrared (FTIR), thermogravimetric analysis (TGA), universal test machine (UTM), field emission scanning electron microscope (FESEM) and atomic force microscopy (AFM) techniques. The resulting nanocomposite membranes exhibited improved stabilities (mechanical and oxidative) and good water retention properties. SPEEK membranes embedded with AIT nanoparticles indicated higher proton conductivity in comparison with pristine SPEEK membrane. This increase is attributed to water channeling at the polymer/nanoparticle interface and connectivity of the water channels which creates more direct pathways for proton transport. Well optimized SPEEK/AIT (2 wt.%) showed 0.065 S cm^{-1} proton conductivity, 38% water uptake and 24% swelling at 25 °C. This membrane showed proton conductivity of 0.12 S cm^{-1} and maximum power density of 204 mW cm^{-2} at 80 °C which indicates its potential application in proton exchange membrane fuel cell (PEMFC). The prepared membranes can be potential candidates for fuel cells and batteries.

1. Introduction

Polymer electrolyte membranes have attracted extensive attention because of potential application in electric powered vehicles

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and portable electronic devices such as fuel cells, batteries and electrolysis [1–5], desalinations and separations [6,7]. Fuel cells directly convert chemical energy into electrical energy. Proton exchange membranes (PEMs) are one of the vital components in polymer electrolyte membrane fuel cells (PEMFCs) and they must have some criteria to be advantageous for application: suitable water uptake, high proton conductivity and good thermal, mechanical and chemical stability [8]. The PEMs serve as the electrode separators and play primary role for conducting protons from the anode to cathode. Perfluorosulfonate ionomer membranes, such as Nafion membranes, are the most commercial membranes used in the PEMFC applications due to their good proton conductivity, presence of pendant sulfonic acid chain and good oxidative stability [9]. However, application of these membranes is restricted by high cost, poor barrier to fuel and limited operation temperature [10]. Accordingly, numerous materials as substitutes for Nafion have been studied up to now. In this regard, much work has been done on the development of sulfonated aromatic polymers such as sulfonated polyimide (SPI) [11], sulfonated poly (ether sulfone) (SPES) [12], sulfonated poly (phenylene oxide) (SPPO) [13] and sulfonated poly (ether ether ketone) (SPEEK) [14].

Among the various polymers studied in literature, SPEEK is considered the most promising one as it can offer adjustable proton conductivity, low cost and excellent chemical and thermal stability [15]. The proton conductivity of SPEEK can be easily controlled by the degree of sulfonation (DS) and DS can be adjusted by sulfonation conditions such as reaction time, temperature and concentration of sulfuric acid [16]. The proton conductivity, water uptake and membrane swelling increase with increase in DS. However excessive membrane swelling of SPEEK due to high DS diminishes mechanical stability and hence shortens the durability of membranes. For practical use, therefore, the SPEEK membranes with high DS (about 70%) should be modified to improve their mechanical and dimensional stability, which might be realized through blending them with inorganic additives. Addition of inorganic nanoparticles to SPEEK generally enhances the mechanical properties of the hydrated membranes. But, the proton conductivity may decline when nanoparticles are aggregated [17,18]. Recently, the authors prepared new proton conducting composite membranes based on nanoporous silica containing phenyl sulfonic acid or propyl sulfonic acid [19], $BaZrO_3$ nanoparticles [20], Sulfonated graphene oxide nanoplatelets [21,22] and iron titanate (IT) nanoparticles [23,24] for polymer electrolyte membrane fuel cells (PEMFCs). Many researches have been done on the nanocomposite membranes based on SPEEK [25–27]. But, synthesis of SPEEK/amine-functionalized iron titanate (AIT) for using as electrolyte in PEMFCs and its performance have not been reported elsewhere yet.

This study involves the use of the AIT nanoparticles as fillers in nanocomposite membranes and its enhanced performance evaluations such as proton conductivity, water uptake, mechanical properties, oxidative stability and power density. The hydrogen bonds between hydroxyl and amine groups of AIT nanoparticles and free water molecules augmented proton conductivity of nanocomposite membranes with Vehicle mechanism [28]. Also, the —NH_2 groups of AIT nanoparticles provided hydrogen bonding interactions with —SO_3H groups of the polymer matrix and increased the mechanical stability of nanocomposite membranes. Furthermore, amination of IT nanoparticles decreased the aggregation of nanoparticles and increased proton conductivity of membranes by a decrease in separation distance between AIT nanoparticles. The hydroxyl groups of IT nanoparticles reacted with alkoxy groups of 3-aminopropyltriethoxysilane (APTES) and increased the rate of iron titanate nanoparticles dispersion and compatibility in SPEEK matrix as well [29]. The chemical structure, morphology, membrane swelling, water uptake, mechanical properties, thermal/oxidative stability and proton conductivity of the membranes were investigated and the PEM performance was measured for PEMFCs.

2. Experimental section

2.1. Materials

Poly (oxy-1, 4-phenyleneoxy-1, 4-phenylenecarbonyl-1, 4-phenylene), PEEK, (molecular weight, 20,800 g mol^{-1}) was used as supplied by Sigma–Aldrich. Triethyl amine (99%, Merck) and 3-aminopropyltriethoxysilane, APTES, (98%, Merck) were used as surface grafting catalyst and silane coupling agent, respectively. Other materials and solvents (Merck) were used without further purification.

2.2. Synthesis of AIT nanoparticles

IT nanoparticles were prepared by our research group according to the literature procedure [30]. An appropriate amount of stearic acid was melted in a beaker at 73 °C, then a 0.1 mol of iron acetyl acetonate was added to it and dissolved to form a transparent brown solution. 0.05 mol tetrabutyl titanate was added to the solution and stirred to form a homogeneous brown sol. It was cooled in a way that its temperature slowly was decreased to room temperature, then it was dried in an oven at 80 °C for 12 h to obtain dried gel. The final gel was calcinated for 4 h at 900 °C in air atmosphere to obtain IT particles. Size of nanoparticles was obtained below 80 nm.

IT nanoparticles were activated in a 10% (w/w) HCl solution for 3 h for hydroxyl regeneration. 1 g of activated IT nanoparticles was kept in a vacuum oven for 24 h at 100 °C and then dispersed in 100 mL anhydrous toluene using ultrasonication for 30 min. Then, 0.3 mL of triethyl amine and 4 mL of APTES were added drop-wise to the mixture. The solution was then refluxed under N_2 atmosphere at 80 °C, washed several times with toluene and ethanol to remove excess reactants, then it was dried in the oven at 80 °C for 24 h. Fig. 1 briefly illustrates the above mentioned procedure.

2.3. Membrane preparation

PEEK polymer was sulfonated by direct sulfonation with sulfuric acid. First, 5 g of PEEK was dissolved in concentrated sulfuric acid and stirred for 1 h at room temperature. The temperature of

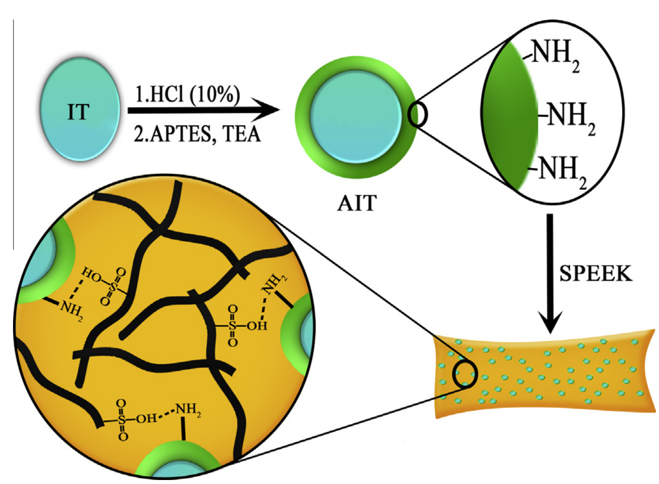

Fig. 1. Schematic representation for functionalization of IT nanoparticles and their dispersion in SPEEK matrix.