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Effect of functionality of polyhedral oligomeric silsesquioxane [POSS] on the properties of sulfonated poly(ether ether ketone) [SPEEK] based hybrid nanocomposite proton exchange membranes for fuel cell applications

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ABSTRACT

Organic–inorganic hybrid nanocomposite membranes were prepared using three different types of POSS i.e., PEG POSS® cage mixture (PPOSS), trisilanol phenyl POSS® (TSP POSS) and trisulfonic acid isobutyl POSS® (SPOSS) at a fixed loading of 2% (w/w) as filler and SPEEK with degree of sulfonation (DS) 55% as polymer matrix. The influence of POSS functionality on hybrid membrane's thermo-mechanical properties, morphology, water uptake and proton conductivity was investigated. Thermal and mechanical stability of hybrid membranes increased upon incorporation of POSS. The size and distribution of POSS particles into SPEEK matrix was studied using transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) and it was found that TSP POSS and PPOSS based membranes showed smaller particle size and uniform distribution as compared to SPOSS based membranes which consequently affect the water uptake and proton conductivity of these hybrid membranes. The water uptake studies were carried out at three different temperatures i.e. 30, 80, 100 °C for 24 h and POSS based composite membranes showed higher water uptake and proton conductivity compared to neat SPEEK membranes. The highest proton conductivity (64.6 mS/cm) was observed for TSP POSS containing membrane which is more than double of neat SPEEK (31.3 mS/cm) membrane. The composite membrane containing TSP POSS can be considered as suitable membrane for PEMFCs applications.
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1. Introduction

Sulfonated aromatic polymers have been widely investigated as membranes for water purification by reverse osmosis [1] vanadium redox flow batteries for energy storage [2] and fuel cells for energy production [3]. Among different types of fuel cells, polymer electrolyte membrane fuel cells (PEMFCs) offer high fuel utilization efficiency with environmentally

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benign operation [4,5]. The properties of membranes such as proton conductivity, water uptake, mechanical, thermal and chemical stability are primary characteristics important for the fuel cell performance. Perfluorosulfonic acid (PFSA) membranes, state-of-the-art such as Nafion are the most widely used membrane materials in fuel cell applications owing to their high proton conductivity and good chemical stability. But, the problem of high cost and reduced efficiency at elevated temperatures has restricted their widespread application in PEMFC [6–8]. Therefore, the scientific community is intensively involved in finding alternative membrane materials based on different high-performance aromatic polymers functionalized with proton conductive groups [9–12]. But, the performance of most aromatic membranes is not comparable to PFSA membranes, particularly in terms of proton conductivity at low relative humidity (RH) and membrane stability.

Sulfonated poly(ether ether ketone) [SPEEK] has been emerged as a potential candidate owing to have a comparable proton conductivity, superior thermal and chemical properties accompanied with lower fuel crossover. SPEEK is quite durable under fuel cell operating conditions along with a long lifetime of approximately 3000 h [13,14]. With increasing degree of sulfonation (DS), the long term stability of SPEEK is questionable because of the hydroxyl radical initiated degradation of SPEEK. On the other hand, low to medium DS of SPEEK in the range of 45–55% exhibit reasonably good thermo-chemical stability but low values of proton conductivity. SPEEK with high degree of sulfonation can be used to achieve high proton conductivity which in-turn is accompanied by excessive swelling leading to poor mechanical properties of the membrane and hence is undesirable for fuel cell applications. Therefore, a membrane showing an optimum balance of water swelling and proton conductivity would be the most suitable PEM for fuel cells.

A variety of modification approaches such as cross-linking [15–18] and blending [19,20] have been explored to prepare efficient membranes based on SPEEK. The addition of inorganic filler is also one of the most widely used approaches to modify the SPEEK because inorganic additives can withstand relatively higher temperatures than virgin polymer. Different inorganic fillers such as zirconium phosphate [21], titanium [22] silica [23] and nanoclays [24] are used to alter the properties of neat polymer. The presence of functional group on inorganic filler is beneficial to improve polymer filler interaction. Few examples such as: zirconium phosphate sulfophenylene phosphonate [25,26], sulfonated titania [27], sulfonated silica [28] or organically modified clay [29] as inorganic fillers have shown better performance than their unmodified counterparts. The presence of functional groups on filler might generate a variety of interactions such as covalent, ionic, hydrogen bonding etc. with polymer matrix affecting the properties of composite. The purpose of such modifications was to suppress the methanol permeation while keeping the high values of proton conductivity. But in case of hydrogen fuel cell, the main aim to add functional filler is to retain water at higher temperatures to maintain higher values of proton conductivity.

In search of potential filler for PEMFCs, polyhedral oligosilsesquioxane (POSS) has been emerged as very attractive filler. POSS could be regarded as a hybrid nanoparticle since it has a well-defined cube-octameric siloxane skeleton (about 1–3 nm in size) with eight organic vertex groups, one or more of which are reactive or polymerizable. These particular structural features render POSS to be a versatile additive for acquiring enhanced thermo-mechanical properties, better thermal stability, oxidative resistance and abrasion resistance [30–42]. The interaction of POSS with polymer matrix usually depends on various factors such as the size of POSS cage, nature of organic periphery, number and type of reactive functional groups and the amount of POSS incorporated into polymer matrix. Further, the size and distribution of POSS particles into polymer matrix affect the organic–inorganic phase interfacial characteristics to a large extent thereby influencing the properties of nanocomposites [43]. POSS has been studied in different polymer matrix such as SPPSU [44,45] and Nafion [46] and proved to be synergistic filler for fuel cell applications. It is possible to tailor a variety of POSS/polymer composite by varying substitution on POSS [47,48].

Therefore, we found it very crucial and interesting to study the effect of POSS functionality on the properties of SPEEK nanocomposite membranes. The concentration of POSS at 2% (w/w) was optimized in our previous work.

2. Experimental

2.1. Materials

Victrex PEEK (150 XF ICI, USA), sulfuric acid (98% Merck), dimethyl acetamide (DMAc) (Qualigens, India), PEG POSS® Cage Mixture (PPOSS), trisulfonic acid isobutyl POSS® (SPOSS), trisilanol phenyl POSS® (TSP POSS) from Hybrid Plastics, USA were used as received without further purification. The structure of POSS particles is shown in Scheme 1(a)–(c) along with their description in Table 1.

2.2. Synthesis of SPEEK

SPEEK with varying degree of sulfonation was prepared by varying reaction time from 2 to 3 h [49–52]. The detailed procedure of sulfonation and determination of DS is reported in our earlier publications [53,54]. For the present studies, SPEEK with DS ~55% was used as polymer matrix. Ion exchange capacity IEC (expressed in meq/g) of the polymer can be calculated using the degree of sulfonation and the mean molecular mass of the repeat units (equivalent weight). For SPEEK with DS = 55%, equivalent weight is EW = 603, which gives IEC = 1000 DS/EW = 0.9.

2.3. Membranes casting

Solution casting method was employed to prepare homogenous and defect free membranes. SPEEK with DS ~55% and POSS with varying functionality in calculated amounts were dissolved separately in DMAc. The solution of SPEEK and POSS was mixed together and stirred vigorously at room temperature until homogenization and followed by ultrasonication for 30 min. The solution mixture was poured onto glass petridishes followed by solvent evaporation at 80 °C for 12 h.

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