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# Sulfonated fluorinated multi-block copolymer hybrid containing sulfonated (poly ether ether ketone) and graphene oxide: A ternary hybrid membrane architecture for electrolyte applications in proton exchange membrane fuel cells

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ABSTRACT

A ternary hybrid membrane architecture consisting of sulfonated fluorinated multi-block copolymer (SFMC), sulfonated (poly ether ether ketone) (SPEEK) and 1 or 5 wt% graphene oxide (GO) was fabricated through a facile solution casting approach. The simple, but effective monomer sulfonation was performed for SFMC to create compact and rigid hydrophobic backbone structures, while conventional random sulfonation was carried-out for SPEEK. Hydrophilic-hydrophobic-hydrophilic structure of SFMC enhances the compatibility with SPEEK and GO and allow for an unprecedented approach to alter mechanical strength and proton conductivity of ternary hybrid membrane, as verified from universal test machine (UTM) curves and alternating current (AC) impedance plots. The impact of GO integration on the morphology and roughness of hybrid membrane was scrutinized using field emission scanning electron microscope (FE-SEM) and atomic force microscope (AFM). Ternary hybrid showed uniform intercalation of GO nanosheets throughout the entire surface of membrane with an increased surface roughness of 8.91 nm. The constructed ternary hybrid membrane revealed excellent water absorption, ion exchange capacity and gas barrier properties, while retaining reasonable dimensional stability. The well-optimized ternary hybrid membrane containing 5 wt% GO revealed a maximum proton conductivity of 111.9 mS/cm, which is higher by a factor of two-fold with respect to that of bare SFMC membrane. The maximum PEMFC power density of 528.07 mW/cm$^2$ was yielded by ternary hybrid membrane at a load current density of 1321.1 mA/cm$^2$ when operating the cell at 70 °C under 100% relative humidity (RH). In comparison, a maximum power density of only 182.06 mW/cm$^2$ was exhibited by the bare SFMC membrane at a load current density of 455.56 mA/cm$^2$ under same operating conditions.



## 1. Introduction

Fuel cells can minimize the power losses associated with internal combustion engines by converting chemical energy into electrical energy in a single step; they can also alleviate environmental pollution by offering low/zero production of green-house gases [1–4]. Among diverse fuel cells, proton exchange membrane fuel cells (PEMFCs) have been considered the most suitable power sources for portable and stationary electronics due to their high power density, quiet operation and fast start up and shut down [5–8]. Proton exchange membrane (PEM) is a pivotal module of PEMFC that conducts protons from the anode to the cathode and serves as a separator to preclude fuel from coming in contact with the oxidant [9,10]. An ideal PEM should have: (i) rapid proton conductivity, (ii) reduced fuel permeability, (iii) extended morphological stability and (iv) high mechanical modulus and (v) continuous durability with stringent operating conditions [2,11]. In this regard, perfluorosulfonic acid (PFSA) membranes, such as Nafion, are somewhat prosperous candidates because of their high proton conductivity and good thermochemical stability. However, they

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have several inevitable drawbacks, including high cost, high fuel permeability and low proton conductivity at high temperature (>80 °C) and low humidity (<30%) conditions, which hinder the widespread commercial usage of PFSA membranes [12–16]. Consequently, researchers are developing modified PFSA membranes or designing alternative PEMs. A variety of aromatic polymers, especially sulfonated poly (arylene ether ketone), sulfonated poly (ether ether ketone), sulfonated poly (phenylene sulfone) and sulfonated poly (imide), have been extensively explored for PEM applications [17]. However, excess density of sulfonic acid ($SO_3H$) groups in the previously mentioned hydrocarbon polymers result in prompt swelling or hydrogel formation, which are problematic during PEMFC operation [11].

Block copolymerization of a sulfonated hydrophilic oligomer with a fluorinated hydrophobic oligomer has been demonstrated to result a block copolymer with reasonable proton conductivity, dimensional stability and radical resistivity [11]. The ionic clusters in hydrophilic segments potentially offer high ionic conductivity, whereas the C–F bonds in hydrophobic segments afford thermomechanical stability and straightforward synthetic pathway to the block copolymer [17]. Moreover, the generation of well-connected proton conducting channels due to micro-phase separation between hydrophilic and hydrophobic segments further enhanced the proton conductivity without sacrificing mechanical modulus and chemical stability. Bae et al. synthesized a sulfonated poly arylene ether sulfone (SPE) block copolymer containing fluorenyl groups and used it to prepare PEM. The SPE block copolymer membrane exhibited a proton conductivity of 140 mS/cm at 80 °C and 80% RH, which is higher than or comparable to that of Nafion. However, the SPE block copolymer membrane still had reasonable mechanical modulus [18]. Miyake et al. synthesized the sulfonated poly (arylene ether phosphine oxide ketone) (SPA) with different compositions (hydrophobic segments, $X=30$ and hydrophilic segments, $Y=4$, 6 or 8) and employed them for the fabrication of PEMs. It was found that the oxidative stability of X30Y8 membrane increases by a factor of 1.04 over the X30Y4 membrane [12]. Mohanty et al. synthesized the fluorinated sulfonated poly (arylene ether sulfone) (6FBPAQSH-XX) with different degrees of sulfonation and used them for the preparation of PEMs. It was found that tensile strength of 6FBPAQSH-60 membrane decreases by a factor of 1.31 with respect to that of 6FBPAQSH-20. On the other side, it was found that proton conductivity of 6FBPAQSH-60 membrane increases by factors of 8.92 with respect to 6FBPAQSH-20 [19]. Although previously mentioned sulfonated fluorinated multi-block copolymer displayed considerable proton conductivity, the other substantial properties including their mechanical modulus and oxidative stability did not attain the necessities of ideal PEMs. Meanwhile, a variety of membrane reinforcing processes, such as chemical cross-linking, blending an optimal amount of long chain polymers and integration of inorganic additives, have been reported to result in composite PEMs with improved physiochemical, thermomechanical and electrochemical properties.

Recently, carbon nanomaterials including functionalized carbon nanotubes (FCNTs) and GO have been extensively explored for PEM modification owing to their high young's modulus, outstanding physical and chemical properties, aspect ratio and excess ion density [20–22]. Several GO based PEMs were discovered. As instance, Vinothkannan et al. scrutinized the effect of GO content on the properties of SPEEK/SPVdF-HFP membrane. It was found that at 5 wt% GO loading, SPEEK/SPVdF-HFP membrane shows an increase in storage modulus by a factor of 2.02 and in proton conductivity by a factor of 7.78 with respect to SPEEK/SPVdF-HFP membrane [1]. Kumar et al. prepared a Nafion composite membrane with different contents (wt%) of GO for PEMFC applications. By increasing the GO loading from 0 to 6 wt%, the proton conductivity of the membrane increased from 92 to 170 mS/cm, which was ascribed to the interfacial interactions between various sorts of oxygen-related functional groups of GO and Nafion [20]. He et al. introduced GO as filler into a SPI matrix in order to prepare a high performance composite membrane for DMFC applications. The uniform intercalation of GO nanosheets throughout the SPI matrix was achieved by electrostatic interactions between hydrophilic functional groups of GO and SPI, thereby enhancing the water absorption, proton conductivity and mechanical stability of the composite membrane [23].

The intention of the current work was to synthesize a micro-phase separated SFMC. This multi-block copolymer contained fluorinated perfluoropropane biphenyl as a hydrophobic segment and sulfonated poly arylene ether sulfone as a hydrophilic segment. Further, we modified the architecture of the SFMC by integrating SPEEK and GO using a facile and cost-competitive solution casting approach. The constructed membranes including SFMC, SFMC/SPEEK (10 wt%), SFMC/SPEEK (10 wt%)/GO (1 wt%) and SFMC/SPEEK (10 wt%)/GO (5 wt%) are denoted to as SF, SFSP, SFSPG-1 and SFSPG-5, respectively. The effects of blending SPEEK and GO on the overall thermomechanical, morphological, structural, proton conduction and gas barrier properties were explored using appropriate instrumental techniques. The suitability of proposed ternary hybrid membrane toward PEMFC applications was estimated by scrutinizing the performance of single cell containing ternary hybrid at 70 °C under fully hydrated condition.

## 2. Experimental

### 2.1. Materials

4,4′-Bis[(4-chlorophenyl)sulfonyl]−1,1′-biphenyl (BCPSBP), 4,4′-dihydroxybiphenyl (DHBP), decafluorobiphenyl (DFBP), 4,4′-hexafluoroisopropylidenediphenol (HFIP), potassium carbonate ($K_2CO_3$) *N,N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidinone (NMP), tetrahydrofuran (THF) and toluene were purchased from Aldrich Chemicals. Poly (ether ether ketone) powder was purchased from the Victrex Company. Graphite (Gr) powder, potassium permanganate ($KMnO_4$) and sodium nitrate ($NaNO_3$) were procured from the Alfa Aesar Company. Other reagents and solvents were supplied by Duksan Chemical, South Korea, and were used as received.

### 2.2. Synthesis of oligomers

#### 2.2.1. Hydrophilic oligomer

Synthesis of sulfonated BCPSBP was performed based on the procedure reported in the reference [24]. Then, synthesis of hydrophilic oligomer was performed via a nucleophilic substitution reaction using sulfonated BCPSBP, similar to a procedure reported in the reference [11]. In a typical procedure, 3.43 g of $26.8\times10^{-3}$ M $K_2CO_3$, 2.50 g of $13.4\times10^{-3}$ M DHBP, 9.40 g of $12.2\times10^{-3}$ M sulfonated BCPSBP, 23 mL toluene and 17 mL DMAc were taken together in a three-necked round-bottomed flask. The flask was then placed on a hot plate coupled with a Dean-Stark trap condenser, a $N_2$ gas inlet and a magnetic stirrer. Reaction was conducted at 120–140 °C (oil bath) for 9 h to carry-out the nucleophilic substitution reaction. Afterward, the reaction temperature was raised to 160 °C to remove water generated due to the toluene distillation. A pale yellow-color viscous liquid was formed after refluxing at the same conditions for 6 h. This was cooled to room temperature and precipitated in a solvent (methanol/acetone/deionized water, 10:1:1, v:v:v). The resultant solid product was filtered, washed with methanol and dried at 100 °C in oven for 12 h.



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