



# Styrenic block copolymer/sulfonated graphene oxide composite membranes for highly bendable ionic polymer actuators with large ion concentration gradient

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## ABSTRACT

In this study, sulfonated graphene oxide (sGO) with a large enhanced sulfonation degree of  $1.65 \text{ mmol g}^{-1}$  was simultaneously introduced as a highly ion conduction-activating carbonaceous filler for ionic polymer–metal composite (IPMC) actuator. The nanostructured styrenic block copolymer/sGO/ionic liquid (IL) composite membrane actuators revealed much larger actuation performance than top-ranked polyelectrolyte/IL actuators ever reported so far in terms of bending strain (0.88% under 2 V dc), initial strain rate ( $0.312\% \text{ min}^{-1}$ ), and charge-specific displacement ( $276.4 \text{ mm C}^{-1}$ ). Moreover, SSPB/sGO/IL actuators exhibited excellent actuation performance without drawbacks of conventional IPMCs, such as back-relaxation and early loss of inner solvent. In addition, *via* tracking the movement of the IL's anion through energy-dispersive X-ray spectroscopy (EDS) analysis, not only the transporting behaviour of IL but also the pumping effect with solvated ion complexes inside the actuator are confirmed for the first time.

## 1. Introduction

Air-operable ionic polymer–metal composite (IPMC) actuator system in which ionic liquids (ILs) are used as inner solvents instead of existing water, has been increasingly investigated. The IL enables the IPMC actuator to operate stably in air due to its extremely low vapor pressure, wide electrochemical window, high ion conductivity and low viscosity [1–8]. A typical IPMC, composed of a polymer electrolyte membrane sandwiched between a pair of metal electrodes, bends as a result of asymmetric swelling in between both electrodes caused by electrostatic migration of solvated mobile ions under low electric potentials of 1–5 V [9–18]. DuPont's Nafion material is a commonly used polymer electrolyte for IPMC systems that exhibits large and fast bending actuation in its aqueous form. However, the IPMCs based on the hydrated Nafion exhibits fatal drawbacks, including a fast back-relaxation and an early loss of water. Moreover, the IL form shows small

ionic conductivity with resultant low strains owing to the narrow ionic pathways (the size of hydrated ion cluster is smaller than 4 nm) [3,8,19–26].

In previous researches, we have proposed the use of nanostructured polymer electrolyte membranes composed of a poly(*t*-butyl-styrene)-*b*-(ethylene-*r*-propylene)-*b*-(styrene-*r*-styrene sulfonate)-*b*-(ethylene-*r*-propylene)-*b*-(*t*-butyl-styrene) (*t*BS-EP-SS-EP-*t*BS; SSPB) pentablock copolymer instead of the commercial Nafion and an IL [8,27,28]. The SSPB-based IPMCs revealed much superior actuation performance to the Nafion counterparts in terms of displacement, response rate and the energy conversion efficiency of actuation. Following this, sulfonated montmorillonite (sMMT) was introduced into the SSPB matrix [8,28]. The IPMCs based on SSPB/sMMT composite membranes reinforced the actuation performance because the sheet-like morphology of intercalated sMMT particulates facilitates ion migration over the adjacent ionic channels like an ionic bridge in the nanostructured SSPB matrix.

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These previous studies inspired us to introduce composite fillers with greater sulfonation degrees and aspect ratios to further progress the actuation performance, which is in high demand in the real applications. In this study, sulfonated graphene oxide (sGO) with a large sulfonation degree of  $1.65 \text{ mmol g}^{-1}$  (it was  $0.33 \text{ mmol g}^{-1}$  in our previous study [8]) was successfully synthesized as a highly ion conduction-activating carbonaceous filler. This product, with a 2-dimensional geometry of an extremely high aspect ratio, is comparable with the existing surface-modified layered inorganic matters. The actuator revealed a much superior actuation performance to top-ranked ionic polymer/IL actuators aforementioned in terms of displacement, response rate and energy efficiency of actuation, without drawbacks of conventional IPMCs; for instance, the back-relaxation and the early loss of inner solvent. Additionally, via tracking the movement of the IL's anion through energy-dispersive X-ray spectroscopy (EDS) technique, the pumping effect and the transporting behaviour of IL inside the actuator were confirmed for the first time.

## 2. Experiments

### 2.1. Materials

In the experiments, 10 wt% dispersion of poly(*t*-butyl-styrene)-*b*-(ethylene-*r*-propylene)-*b*-(styrene-*r*-styrene sulfonate)-*b*-(ethylene-*r*-propylene)-*b*-(*t*-butyl-styrene) (tBS-EP-SS-EP-tBS; SSPB) pentablock copolymer in a mixed solvent of cyclohexane and heptane (MD-9200, Kraton Polymers) was used. The mixed solvent was exchanged by tetrahydrofuran (THF) before use. The SSPB material revealed an ion exchange capacity (IEC) value of  $2.0 \text{ meq. g}^{-1}$  ( $2.0 \text{ mmol H}^+$  per 1 g polymer). An ionic liquid of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI) was custom-made with a high purity of greater than 99.9% (provided by C-TRI, Korea). A Nafion dispersion (DE-2021,  $0.95 \text{ meq. g}^{-1}$ , DuPont) was engaged as an ionic polymer electrolyte reference. The other reagents were of analytical grade and used without further purification.

### 2.2. Functionalization of GO

Graphene oxide (GO) was prepared using a modified Hummers method reported previously [29]. Sulfonated GO (sGO) was synthesized according to a procedure in the literature [30]. Briefly, 375 mg of GO was dispersed in deionized water through sonication for 1 h in an ultrasonic bath. Next, an aryl diazonium salt was prepared via the reaction of sulfanilic acid (230 mg) and sodium nitrite (90 mg) in deionized water (50 g) with a few drops of 1 M HCl solution in ice bath. The aryl diazonium salt solution was then added into the GO dispersion with stirring in ice bath and reacted for 2 h to obtain sGO. After the reaction, the solution was freeze-dried.

### 2.3. Preparation of SSPB/sGO/IL membranes and IPMCs

A predetermined amount of sGO as a filler was added into *N,N*-dimethylformamide (DMF) solvent, stirred over 5 h and dispersed under sonication. The sGO dispersion was added to a SSPB copolymer dispersion (10 wt% in THF) and sonicated for 10 min, followed by stirring over 5 h. The mixture was then re-dispersed under sonication and the resulting clear dispersion was cast into a Teflon mould and evaporated slowly at room temperature. The resulting membranes were dried at  $50^\circ\text{C}$  overnight to remove the solvent residue and then protonated and cleaned in 2 M HCl solution and deionized water at room temperature for 30 min each, followed by vacuum-drying at  $45^\circ\text{C}$  overnight. IL-embedded IPMCs were constructed through coating both membrane surfaces with platinum electrodes via an electroless plating method (refer to Supporting Information for the detailed procedure). The SSPB/GO/IL-based IPMCs were fabricated through the same procedure explained above. The overall thickness of the IPMCs was controlled to

$0.2 \pm 0.02 \text{ mm}$  for rational comparison.

### 2.4. Characterization

X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe, ULVAC-PHI) was used to determine the concentration of sulfonic groups on sGO. The morphology of the samples was observed with a transmission electron microscope (TEM, Tecnai F20 G2, FEI).

IL uptake was obtained using equation: uptake (wt%) =  $(W_i - W_n)/W_n \times 100$ , where  $W_n$  and  $W_i$  are the weights of neat and IL-impregnated membranes, respectively. For IL uptake experiments, SSPB membranes fully dehydrated in a vacuum oven were weighed to obtain  $W_n$ , then immersed in a mixture of EMIM-TFSI and methanol (IL: methanol = 1: 1, w/w) for 2 days at room temperature, and finally reweighed after evaporation of methanol at  $60^\circ\text{C}$  under vacuum to determine  $W_i$ . Ionic conductivities of SSPB- and Nafion-based membranes were measured with a potentiostat/galvanostat/electrochemical impedance spectroscopy (EIS) instrument (VMP3, BioLogic Science Instruments, France), combined with a custom-made two-probe cell at room temperature and 20% of relative humidity. The tensile examination was carried out using a universal testing machine (H5KT, Tinius Olsen, USA) with a cross header speed of  $20 \text{ mm min}^{-1}$ .

For the electromechanical test, bipolar voltages were applied on the IPMC actuators using the EIS instrument. The displacement measurement was performed using a CCD camera connected to a computer with a data acquisition (DAQ) system (SCB-68, National Instruments, USA). IPMC strips with dimensions of 23 mm by 2.5 mm were vertically fixed to 3 mm length aluminium grip, and thus the actual strips free length was 20 mm. Tip displacement obtained by measuring horizontal displacement of IPMC strips at tip 20 mm away from grip under an applied voltage of 2 V dc for 10 min. Bending strain was calculated by using the equation:  $\varepsilon (\%) = 2DW/(L^2 + D^2) \times 100$ , where  $W$ ,  $D$  and  $L$  denote thickness, displacement and cantilever length from grip to the measured point, respectively. Potentiostatic analysis of the IPMCs was also conducted during the electromechanical examination of IPMC actuators. Charge-specific displacement was the maximum tip displacement (acquired within 10 min under 2 V dc) divided by charge value obtained from potentiostatic analysis.

## 3. Results and discussion

Pristine SSPB, SSPB/GO and SSPB/sGO membranes were fabricated through solution casting process. The chemical structures of SSPB, GO and sGO fillers used in this study are shown in Fig. 1b–d and their characteristics are summarized in Table 1. The SSPB copolymer revealed a well-defined microphase-separated morphology in which the repeating domain spacing ( $d$ ), composed of alternating styrene-rich little dark grey regions (ionic domain) and aliphatic EP-rich light grey regions (non-ionic domain), was 43.5 nm, and the average diameter of the ionic channel regions was ca. 22 nm, as shown in Fig. 1f and g. Fillers GO and sGO were introduced into SSPB block copolymer with a series of filler content (0.1, 0.5, and 1.0 wt%). The sGO was composed of few stacked layers with a size range of 0.5–5  $\mu\text{m}$  (Fig. 1e). In the TEM images of composites (Fig. 1f and g), sGO exists as a dark filler. The concentration of sulfonic groups in the sGO sample was assessed through X-ray photoelectron spectroscopy (XPS) data (refer to Fig. S1, Supporting Information for the XPS spectra of GO and sGO). The GO spectroscopy results revealed 2 peaks (168.4 eV for S  $2p_{3/2}$  and 169.6 eV for S  $2p_{1/2}$ ) assigned to oxidized sulfur moieties [28,31,32]. The oxidized sulfur moieties were formed during a synthesis step using sulfuric acid. Meanwhile, other 2 peaks (167.3 eV for S  $2p_{3/2}$  and 168.5 eV for S  $2p_{1/2}$ ) with the GO peaks were observed for sGO. The new peaks were from benzenesulfonic groups newly formed on the GO during the sulfonation reaction [33,34]. Thus, it could be estimated that the concentration of benzenesulfonic group on the sGO sample was  $1.65 \text{ mmol g}^{-1}$ . The detailed XPS data are summarized in Table 1.

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