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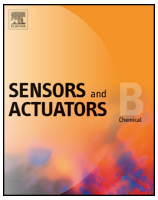

Ionic polymer actuator based on anion-conducting methylated ether-linked polybenzimidazole

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ABSTRACT

A new type of ionic polymer actuator based on anion-conducting methylated poly[(1-(4,4′-diphenylether)-5-oxybenzimidazole)-benzimidazole] (PBI–OO) membranes and a carbon composite electrode material was successfully developed. The anion-conducting membrane was prepared through *N*-methylation of PBI–OO with iodomethane. The ion exchange reaction of the methylated PBI–OO membrane to various anions largely affected the ion conductivity and the resulting actuator performance. The methylated PBI–OO membranes possessed unique small ion clusters with the size of 1.71–2.04 nm and exhibited high tensile moduli and strengths in the hydrated states (tensile modulus: 553 MPa, tensile strength: 32 MPa in the iodide form) due to the π–π stacking interaction among the benzimidazole rings in the polymer backbone. The actuators based on PBI–OO bent toward the negatively charged electrode direction reverse to the bending direction of conventional ionic polymer actuators with cation-conducting membranes. They also revealed exceptional charge-specific blocking forces (at least 17 times larger than those of Nafion-based actuators) because of a combinatorial effect of the larger modulus of PBI–OO-based actuators and the smaller size of ion clusters inside the PBI–OO layer, and the electrolysis of water restrained using a carbon electrode as well. Moreover, the actuators showed no back relaxation within the examined time period even under a high dc voltage beyond the electrolysis voltage of water. The distinct characteristics of the PBI–OO-based actuators are expected to be used as a unique anion-conducting polymer actuator.

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1. Introduction

Ionic polymer actuators constitute a fast growing type of devices in robotics, biomimetics, energy, and automobile sectors because of their unique advantages, including their large, fast, and soft bending actuation under fairly low actuation voltages (1–5 V) [1,2]. A typical ionic polymer actuator consists of an ionic polymer membrane sandwiched between a pair of electrodes. Usually, ionic polymer membranes contain mobile ions, such as lithium cations, and a polar solvent, for example water, to enhance ion mobility. Asymmetric diffusion of hydrated cations toward the negatively charged electrode side under electric potentials is responsible for the low-voltage-driven bending actuation toward positively charge electrode direction [3,4]. The commercial polymer of Nafion from DuPont is the most popular ionic polymer in the ionic polymer actuators field because of its high proton conductivity and robust thermochemical and mechanical stabilities originating from its unique perfluorinated chemical structure [5,6]. However, Nafion-based actuators have fatal drawbacks; they show rapid back relaxation and require constant humidification to prevent drying of Nafion [6–9]. In the last decade, therefore, many studies were focused on the replacement of Nafion. To date, various ionic polymers have been synthesized and tested as the polymer electrolyte of ionic polymer actuators [3,4,6–13]. Among them,

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ion-conducting block copolymers are recognized as promising next generation polymer electrolytes of ionic polymer actuators due to their mechanical stability, dimensional stability against solvents and excellent ion conductivity that stems from the well-organized microphase-separated structure. More importantly, their physical properties are easily tuned by means of controlling the length of each block unit and the total molecular weight [10,13]. Representative examples are sulfonated polystyrene-*b*-poly(ethylene-*co*-butylene)-*b*-polystyrene triblock copolymer [10], polystyrene sulfonate-*b*-polymethylbutylene diblock copolymer [11], and poly(*tert*-butyl-styrene)-*b*-poly(ethylene-*ran*-propylene)-*b*-poly(styrene-*ran*-styrene sulfonate)-*b*-poly (ethylene-*ran*-propylene)-*b*-poly(*tert*-butyl-styrene) pentablock copolymer [12,13]. Most of such ionic polymers are cation-conducting polymer membranes because cations diffuse faster than anions with similar van der Waals radius [14].

Very few papers report the use of anion-conducting polymers for ionic polymer actuators [15–17]. Asaka and Fujiwara reported an anion-conducting polymer actuator constructed with a commercial hydrocarbon polymer with quaternized ammonium groups in 2003 [15]. In 2006, Jeong et al. synthesized a copolymer of fluoroalkyl methacrylate and 2-(dimethylamino)ethyl methacrylate, quaternized the amine groups and fabricated an actuator using the synthesized polymer [16]. Recently, Lee et al. reported polymer actuators with three different grades of commercially available anion-conducting hydrocarbon membranes (Neosepta-AMX, AHA, and AFN) [17]. Despite these endeavors, the performance of anion-conducting polymer is still limited.

Herein, we demonstrate the manufacturing of an anion-conducting polymer, partially methylated poly[(1-(4,4′-diphenylether)-5-oxybenzimidazole)-benzimidazole] (PBI–OO) (Fig. 1) as a polymer electrolyte for ionic polymer actuators. Ionic polymer actuators based on methylated PBI–OO membranes were fabricated via painting carbon-paste electrodes on both sides of the membrane. The partially methylated PBI–OO membranes showed outstanding mechanical properties (tensile modulus of 553 MPa, tensile strength of 32 MPa in the iodide form) in the hydrated states, regardless of the type of exchanged anions (I^-, $CO_3{}^{2-}$, Br^-, CH_3COO^-, and $NO_3{}^-$), and were featured by small ion clusters (1.71–2.04 nm) inside the membranes. The bending actuation was toward the negatively charged cathode direction reverse to the bending direction of conventional ionic polymer actuators with cation-conducting membranes [1,2,5–10]. Without back relaxation during actuation, the methylated PBI–OO actuators produced robust charge-specific blocking forces of at least 17 times greater than Nafion-based actuators, suggesting that the origin of the enhancement could be a synergistic effect of the larger modulus of PBI–OO and the small size of ion clusters inside methylated PBI–OO.

2. Materials and methods

2.1. Materials

Poly[(1-(4,4′-diphenylether)-5-oxybenzimidazole)-benzimidazole] (PBI–OO, Fumion AO) with the weight-average molecular weight (M_w) of greater than 40,000 g mol^{-1}, was purchased from Fumatech. Salts (sodium carbonate, sodium acetate, sodium nitrate, and potassium bromide) as ion-exchange reagents and sodium hydride, iodomethane, and solvents were reagent grade and obtained from Sigma or Daejung and used without further purification. An activated carbon (YP-50F) and a conductive carbon black (Super P) were obtained from Kuraray Chemical and TIMCAL Graphite & Carbon, respectively.

2.2. Synthesis of partially methylated PBI–OO

Partially methylated PBI–OO was synthesized via a procedure reported in the literature (see Fig. 1) [18]. In brief, PBI–OO was dissolved in *N*-methyl-2-pyrrolidone (NMP) at 160 °C. Then, sodium hydride (2 equivalents) was added to this solution at 90 °C, stirred for 1 h and cooled down to room temperature. An excess of iodomethane was then added and reacted at room temperature for 36 h. The methylated polymer was precipitated through pouring the reaction solution into acetone; recovered using filtration and washing repeatedly with acetone until the solution became colorless to remove excess iodomethane and NMP. After washing with acetone, the polymer was washed again in agitated deionized water for 1 day and then dried in vacuum. The partially methylated PBI–OO possessed iodide (I^-) as the counter ion and the degree of methylation determined by ^{1}H NMR was observed as 70% (refer to Fig. S1 in Supplementary Data for the ^{1}H NMR spectrum).

2.3. Preparation and ion exchange of membranes

The methylated I^--form PBI–OO polymer powder was dissolved in dimethyl sulfoxide (DMSO) at room temperature. After complete dissolution, the solution was filtered through a polytetrafluoroethylene syringe filter (pore size: 0.45 μm). The filtered solution was then cast onto a Petri dish (inner diameter: 20 cm) and dried in vacuum. Ion exchange process of the obtained cast membrane was conducted at room temperature via immersion of the membrane in 0.5 M solutions of sodium or potassium salts containing the respective targeting anions (sodium carbonate, potassium bromide, sodium acetate, and sodium nitrate) for 24 h. Finally, the carbonate ($CO_3{}^{2-}$), bromide (Br^-), acetate (CH_3COO^-), and nitrate ($NO_3{}^-$) – form membranes were immersed in deionized water overnight to remove excess salts.

2.4. Fabrication of actuators

First, a carbon-based slurry, as an electrode material for the ionic polymer actuators, was prepared using the following procedure, because it was impossible to perform platinum electroless plating on the PBI–OO membrane owing to the difficulty in impregnation of the positively charged platinum metal ion precursor into the anion-conducting PBI–OO matrix. A 10 wt% methylated I^--form PBI–OO solution in DMSO, activated carbon, and conductive carbon black (300, 100, and 6.25 mg, respectively) were mixed, stirred, and sonicated for 1 h. After that, 160 mg of DMSO was added to the mixture, stirred, and sonicated for 30 min to complete production of the carbon-based slurry. Ionic polymer actuators were fabricated through painting of the carbon-based slurry using a painting brush on both sides of the pre-dried methylated I^--form PBI–OO membrane with dimensions of 5 cm × 3 cm, which was surface-roughened biaxially with a #800 silicon carbide paper before painting to strengthen the physical adhesion between membrane and electrode, followed by drying in vacuum. The surface resistance of carbon composite electrode was ca. 1–2 kΩ. Finally, strips of the electrode-coated membrane were ion-exchanged using the same procedure as that for the ion exchange of the pristine membrane, then were cut to the size of 23 mm × 2.5 mm each to complete the fabrication of actuators and stored in deionized water prior to use.

2.5. Characterization methods

Ion conductivity of the membranes was measured with a potentiostat/galvanostat/electrochemical impedance spectroscopy (EIS) instrument (VMP3, BioLogic Science Instruments), combined with a custom-made two-probe cell, at 25 °C and 22% RH. Tensile modulus was determined using universal testing machines

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