

Supporting Information

High-strain air-working soft transducers produced from nanostructured block copolymer ionomer/silicate/ionic liquid nanocomposite membranes

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1. Functionalization and characterization of MMT

1.1. Functionalization procedure

1.1.1. Protonation of MMT

Figure S1 illustrates the functionalization process of layered silicate. The functionalization of montmorillonite (MMT) was completed through the following procedure. First, raw MMT (Na^+ -MMT; Cloisite Na^+ , Southern Clay Products) was converted into H^+ -MMT via stirring with abundant 1 N H_2SO_4 solution at room temperature for 12 h.

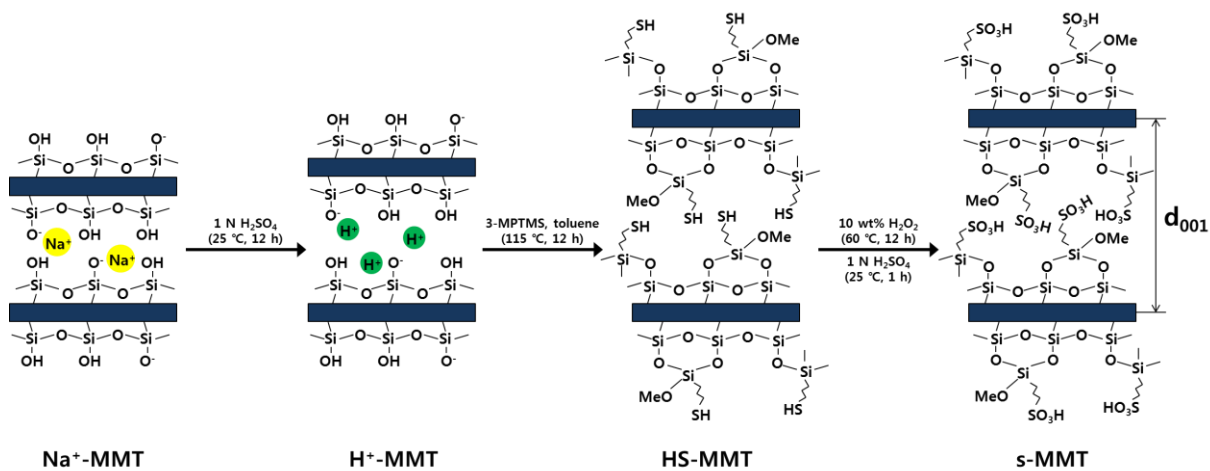
1.1.2. Grafting of organosilane (3-MPTMS) on MMT

Grafting of 3-mercaptopropyltrimethoxy silane (3-MPTMS) on the surface of MMT was then performed at the refluxing temperature of toluene (115 °C) for 12 h, followed by filtering and washing with toluene and vacuum drying at 70 °C for 3 h. The weight ratio of MMT, 3-MPTMS, and toluene was 1:0.2:16 in the mixture of reactants.

1.1.3. Oxidation/Protonation of MMT

The dried powder was agitated in 10 wt% H_2O_2 solution at 60 °C for 12 h to oxidize the grafted thiol groups into sulfonic groups, followed by filtering and washing with a deionized water/ethanol mixture and vacuum drying at 70 °C for 3 h. The obtained particles were stirred in 1 N H_2SO_4 solution at ambient temperature to complete protonation and then filtered and washed with deionized water and ethanol, and dried at 70 °C overnight.

Figure S1. Schematic representation for the functionalization of layered silicates.

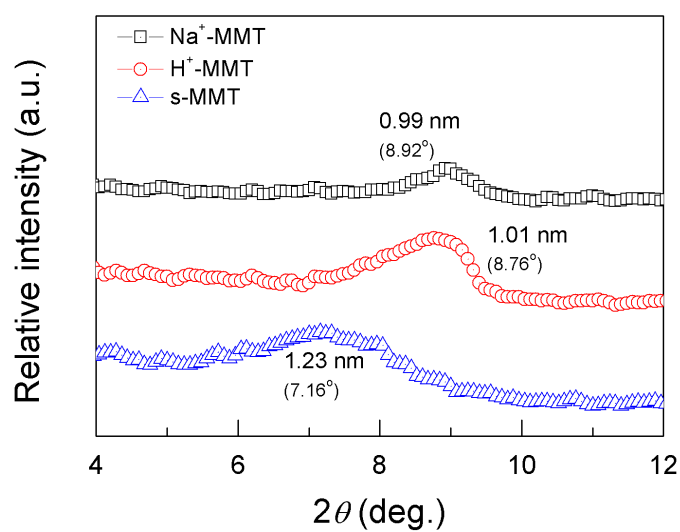


1.2. Wide angle X-ray diffraction (WAXD)

The wide angle X-ray diffraction (WAXD) patterns of Na⁺-MMT, H⁺-MMT and s-MMT are shown in Figure S2. The basal layer spacing (d_{001} spacing) of MMT was evaluated with Bragg's equation ($2d \sin\theta = \lambda$). As reported in the literature [C. H. Rhee, H. K. Kim, H. Chang, J. S. Lee, Chem. Mater. **2005**, 17, 1691; Y. K. Kim, J. S. Lee, C. H. Rhee, H. K. Kim, H. Chang, J. Power Sources **2006**, 162, 180], Na⁺-MMT and H⁺-MMT had d_{001} spacings of 0.99 nm and 1.01 nm, corresponding to 2θ values of 8.92° and 8.76°, respectively. Meanwhile, the interlayer spacing of s-MMT was estimated to be 1.23 nm (2θ value of 7.16°), which was larger than those of Na⁺-MMT and H⁺-MMT. Thus, it was concluded that the sulfonation reaction of MMT took place in the interlayer space of MMT as well as on its external surface.

Figure S2. WAXD patterns of Na⁺-MMT, H⁺-MMT, and s-MMT. The data were obtained using a X-ray diffractometer (XRD, D/Max-2200, Rigaku Denki), under 40 kV and 30 mA of Cu K α radiation with a characteristic wavelength of 0.154 nm and a scanning rate of 4° min⁻¹.

1.



1.3. Thermogravimetric analysis (TGA) and energy-dispersive X-ray spectroscopy (EDS)

The number of grafted sulfonic acid groups per silicate unit weight for s-MMT was measured through thermogravimetric analysis (TGA) and energy-dispersive X-ray spectroscopy (EDS) techniques, which are shown in Figures S3 and S4, respectively. All samples were fully dried prior to the examinations. The thermogravimetric analysis (TGA) was performed in the temperature range of 100–180 °C with a baseline from unmodified H⁺-MMT because the thermal degradation of sulfonic acid groups mostly occurs in that temperature range [C. H. Rhee, H. K. Kim, H. Chang, J. S. Lee, Chem. Mater. **2005**, 17, 1691]. The weight loss in the range of temperature was 2.65 wt% with respect to the baseline of the unmodified MMT; thus, the amount of grafted sulfonic groups on the s-MMT could be estimated to be 0.33 mmol g⁻¹. From the EDS analysis, 0.15 mmol g⁻¹ was registered with the identical sample.

Figure S3. Thermogravimetric analysis traces of H⁺-MMT and s-MMT. This experiment was performed using a thermogravimetric analyzer (TG 209 F3 Tarsus, Netzsch, Germany), with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

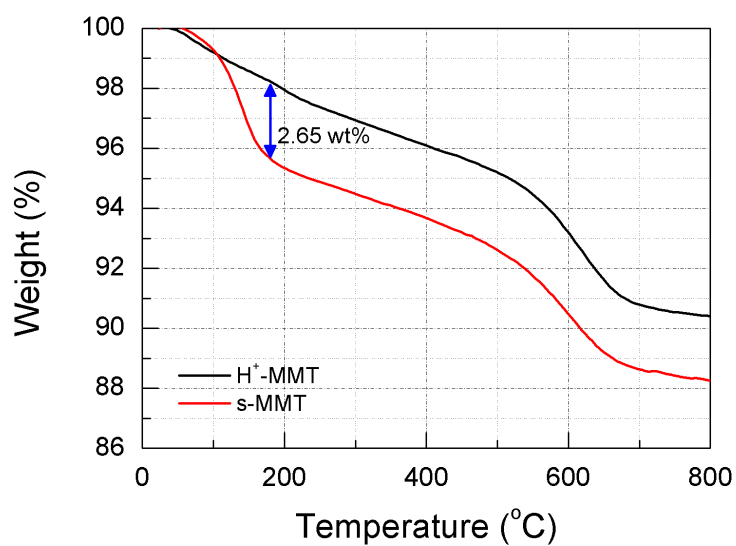
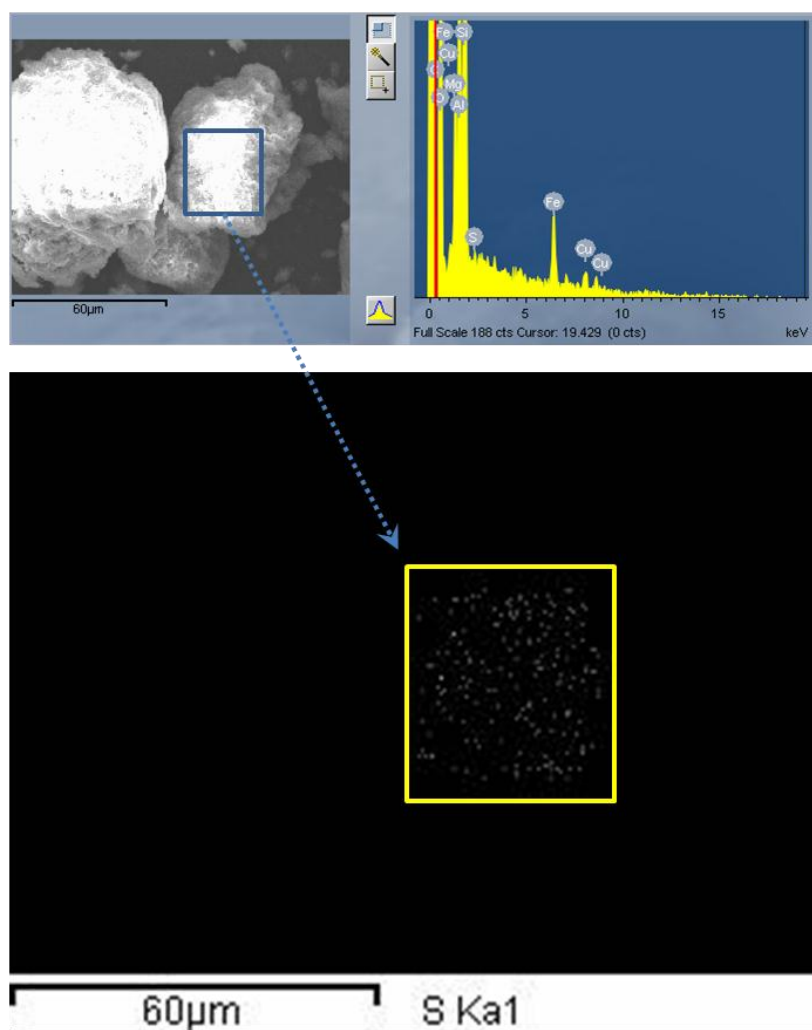


Figure S4. EDS results of s-MMT. A scanning electron microscope (SEM, JSM-6380, Jeol, Japan) combined with an energy-dispersive X-ray spectrometer (INCA X-Act, Oxford Instruments, UK) was used in this analysis. Sulfur atom was detected on the surface of sulfonated silicates.



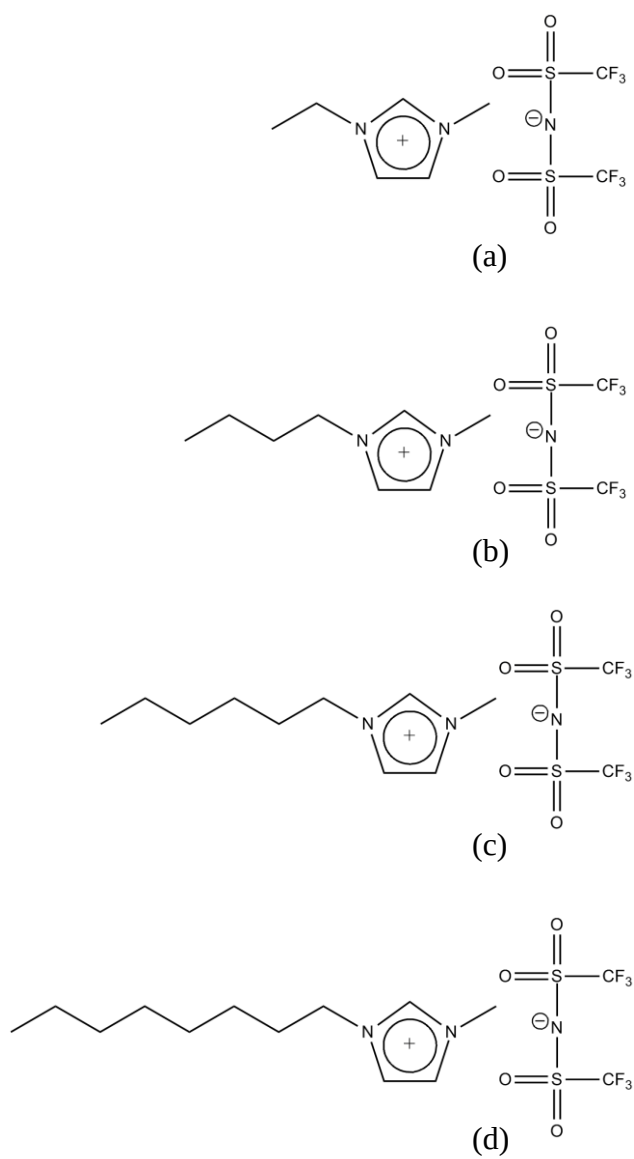
1.4. Back titration

Ion exchange capacity (IEC; milliequivalent (meq) of H^+ per g of silicate) was also assessed through a typical back-titration procedure. 0.5 g of silicates was soaked in a mixture of 45 ml deionized water and 5 ml 0.1 M NaOH solution overnight. Then, the remaining NaOH was titrated with 0.1 M HCl solution after adding a few drops of a 0.1% phenolphthalein indicator. The IEC values were obtained through subtracting the added volume of HCl solution from the initial NaOH volume. The sulfonation of MMT revealed almost invariable IEC upon the sulfonation reaction (H^+ -MMT: 0.91 meq g^{-1} , which is in good agreement with 0.926 meq g^{-1} provided from the manufacturer; s-MMT: 0.89 meq g^{-1}). The sulfonation reaction of MMT with 3-MPTMS seems not to contribute to the increase in IEC because of the inherently large IEC value of the natural MMT.

2. Chemical structures of ionic liquids (ILs)

The four imidazolium-based ILs (C2, C4, C6, and C8) have the same bis(trifluoromethylsulfonyl)imide (TFSI) anion but a different imidazolium cation with different lengths of the linear hydrocarbon substituent on the N(1) position of the imidazolium cation, as shown in Figure S5. The number in the sample codes of ILs denotes the number of carbon in the hydrocarbon substituent. Thus, the bulkiness of cation increases with the increase in carbon number of the hydrocarbon substituent.

Figure S5. Chemical structures of ionic liquids: a) C2, b) C4, c) C6, and d) C8 ILs.



3. Fabrication of IL-embedded IPMCs

3.1. Preparation of IL-free IPMCs

IL-free IPMCs were produced from covering both membrane surfaces with platinum electrodes via electroless plating. First, a strip of SSPB or its clay nanocomposite membrane was roughened biaxially with a #1000 silicon carbide paper to strengthen the physical adhesion between membrane and electrode. Then, the membrane was cleaned via sonication, and subsequently washed with 3 wt% H_2O_2 and 2 N HCl solutions, and deionized water at 80 °C, each for 30 min. After that, the pretreated membrane was immersed in 0.01 N $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ aqueous solution overnight at room temperature to exchange protons with Pt ions. The membrane was rinsed with deionized water, placed in 180 ml of stirring deionized water at 40 °C, and then 2 ml of 5 wt% NaBH_4 and 2 ml of 5 wt% NH_4OH aqueous solutions were added every 30 min while increasing the temperature gradually up to 60 °C in 3.5 h. Subsequently, 4 ml of the NaBH_4 solution was added every 30 min for 2 h at 60 °C. This deposition procedure was repeated 3 times, which led to the electrode thickness of approximately 5 μm and the corresponding surface resistance of 4 ~ 9 Ω . The resulting Pt-plated membranes were immersed in 1 N LiOH aqueous solution for 12 h to complete the IL-free IPMC production process.

3.2. Impregnation of IPMCs with ILs

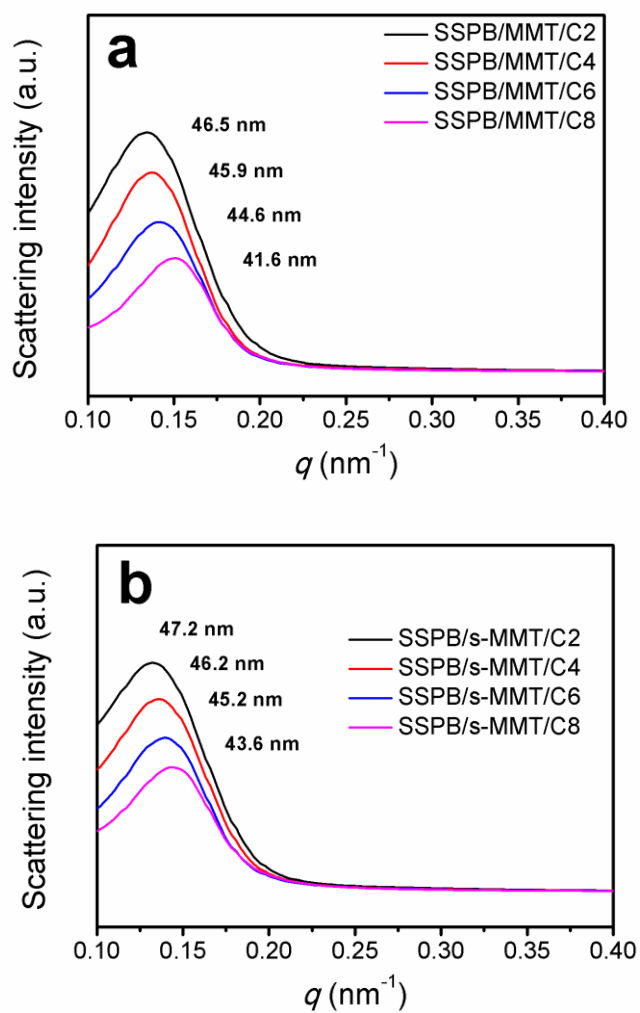
For completion of IPMCs based on nanostructured block ionomer/silicate/ionic liquid membranes, the IL-free IPMCs were soaked in each mixture of methanol and C2, C4, C6, or C8 IL (see the chemical structures of ILs in Figure S5) (methanol:IL = 1:1, w/w) for 2 days at room temperature, followed by evaporation of methanol at 60 °C under vacuum.

4. Characterization of IL-embedded membranes and their IPMCs

4.1. Small angle X-ray scattering (SAXS)

Figure S6 shows SAXS profiles of SSPB/MMT/IL and SSPB/s-MMT/IL membranes with a series of ILs (C2, C4, C6, and C8). The incorporation of silicates (8 wt% of MMT and s-MMT) into SSPB matrix further extended the spacing to a limited extent, especially with s-MMT. From the SAXS examination, it could be confirmed that regardless of the existence of silicate and its surface modification, the spacing of the IL-incorporated SSPB membranes monotonously decreased with increasing carbon number on the N(1) position of the imidazolium ring of IL, although the amount of IL uptake in the SSPB matrix was in the reverse order. This indicates more selective swelling towards the ionic domain in the SSPB matrix in the case of ILs with shorter hydrocarbon substituent on the imidazolium ring of IL, resulting from its higher hydrophilicity.

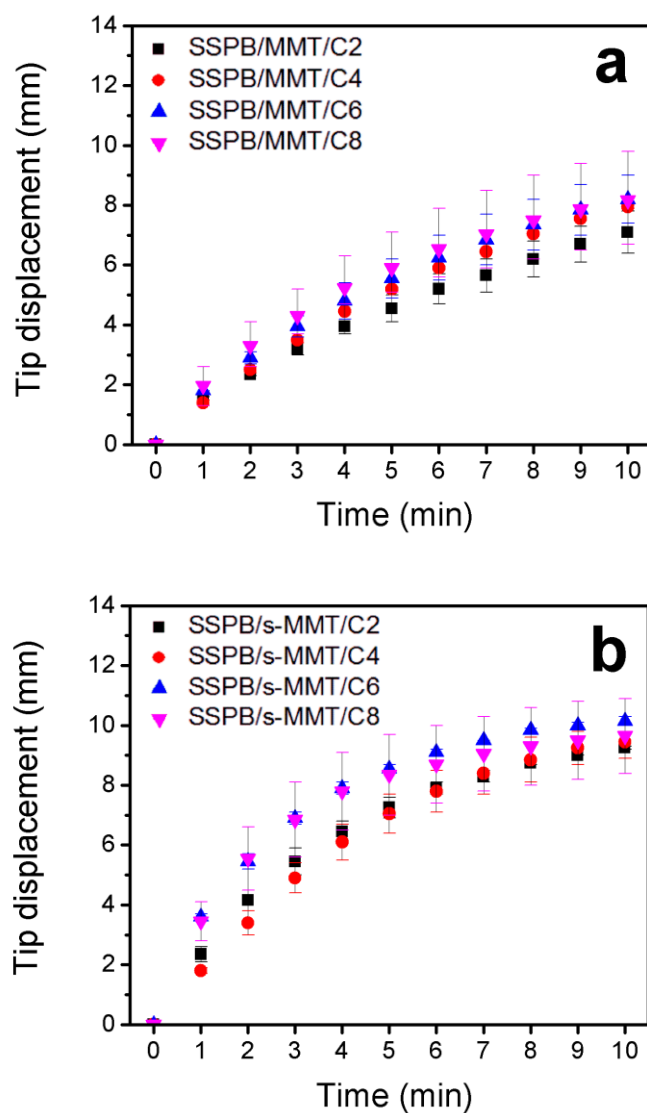
Figure S6. SAXS profiles of: a) SSPB/MMT/IL and b) SSPB/s-MMT/IL membranes with a series of ILs (C2, C4, C6, and C8).



4.2. Actuation performance

Figure S7 exhibits tip displacement vs. time curves of SSPB/MMT/IL and SSPB/s-MMT/IL IPMCs with a series of ILs (C2, C4, C6, and C8). The nanocomposite membranes as polymer electrolytes of the IPMCs had the silicate content of 8 wt%. The electromechanical response was evaluated by measuring the horizontal displacement at the tip of cantilever (free length: 20 mm) under 2 V dc during 10-min bending actuation. Compared with the SSPB/IL and SSPB/MMT/IL IPMCs, the SSPB/s-MMT/IL IPMC revealed the largest bending displacement and the fastest response rate. The bending displacements of the SSPB/MMT/IL and SSPB/s-MMT/IL IPMCs revealed the same tendency as that of the SSPB/IL IPMC on the actuation performance order ($C8 \approx C6 > C4 > C2$). In addition, all examined IPMCs did not show any evidence of back relaxation during the actuation period of 10 min, while revealing much superior bending actuation performances to the Nafion counterpart in terms of bending displacement and response rate.

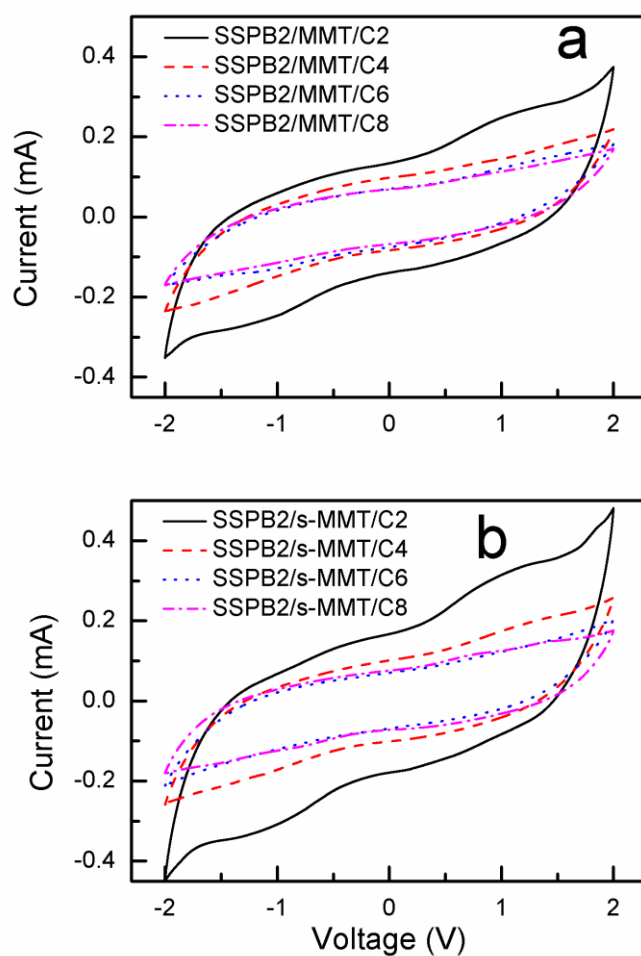
Figure S7. Tip displacement vs. time curves of: a) SSPB/MMT/IL and b) SSPB/s-MMT/IL IPMCs with a series of ILs (C2, C4, C6, and C8). The bending actuation test was carried out under an applied voltage of 2 V dc. The nanocomposite membranes as polymer electrolytes of the IPMCs had the silicate content of 8 wt%. IPMC strips with dimensions of 23 mm in length and 3 mm in width were vertically fixed to 3 mm length by a platinum grip, and thus the actual free length of the strips was 20 mm. The tip displacement was obtained by measuring the horizontal displacement of IPMC strips at the tip of 20 mm away from the grip.



4.3. Cyclic voltammetry (CV)

Figure S8 displays cyclic voltammograms of IPMCs based on SSPB/MMT/IL and SSPB/s-MMT/IL membranes with a series of ILs (C2, C4, C6, and C8). The CV measurement was carried out via a two-electrode system with a potential range of $-2 \sim 2$ V and a scan rate of 50 mV s^{-1} . No faradic current was observed in the CV profiles within the examined potential range. This means that no electrolysis of the imidazolium ILs in the potential range occurred. Shorter linear hydrocarbon substituents on the N(1) position of the imidazolium cation of IL resulted in higher capacitances in the SSPB-based IPMCs because of less bulkiness of the corresponding IL cations, leading to more charging at the interface between electrolyte and electrode. Meanwhile, both SSPB/MMT/IL and SSPB/s-MMT/IL IPMCs overall revealed smaller capacitances than the SSPB/IL IPMC possibly because of steric hindrance from the intercalated silicates in the SSPB matrix.

Figure S8. Cyclic voltammograms of IPMCs based on: a) SSPB/MMT/IL and b) SSPB/s-MMT/IL membranes with a series of ILs (C2, C4, C6, and C8). The CV measurement via a two-electrode system was performed by connecting the counter- and reference-electrode leads to one side of the IPMC and by connecting the working-electrode lead to the other side, with a potential range of $-2 \sim 2$ V and a scan rate of 50 mV s^{-1} .



5. IL and water uptakes of membranes

The value of uptake was obtained by the following equation: uptake (wt%) = $(W_i - W_n)/W_n \times 100$, where W_n and W_i are the weights of the neat and IL- or water-impregnated membranes, respectively. For the IL uptake experiment, SSPB membranes fully dehydrated in a vacuum oven were weighed to obtain W_n , then immersed in each mixture of IL/methanol (IL:methanol = 1:1, w/w) for 2 days at room temperature, and finally reweighed after evaporation of methanol at 60 °C under vacuum to determine W_i . For the assessment of water uptake, the SSPB membranes fully swollen in deionized water for 1 day at room temperature were wiped with a clean filter paper, and then reweighed immediately to determine W_i . The resulting data were summarized in Table S1.

Table S1. IL and water uptakes of SSPB/IL, SSPB/MMT/IL, SSPB/s-MMT/IL, and Nafion/IL

Membrane	Ionic liquid	IL uptake (wt%)	Water uptake (wt%)
SSPB/IL	C2	81	-
	C4	98	
	C6	112	
	C8	126	
SSPB/MMT/IL ^a	C2	95	-
	C4	108	
	C6	125	
	C8	142	
SSPB/s-MMT/IL ^a	C2	103	-
	C4	114	
	C6	130	
	C8	150	
Nafion/IL	C2	48	-
	C4	59	
	C6	100	
	C8	123	
SSPB/water	-	-	156
SSPB/MMT/water ^a	-	-	169
SSPB/s-MMT/water ^a	-	-	166
Nafion/water	-	-	25

^a The silicate content in the nanocomposites was fixed at 8 wt%.

6. Membrane-thickness control and summary of the resulting thickness values

The thickness of membrane was controlled using a bar coater (Comate 3000VH, KIPAE Engineering and Technology). The thickness control was achieved by manipulating the height of doctor blade from the bottom substrate. Other machine factors (the sliding speed of doctor blade, the kind of substrate, the temperature of bottom substrate, and the drying speed) were also optimized to give high-quality membranes with a controlled thickness (0.23 ± 0.02 mm). The detailed conditions for the fabrication of membranes in this study were as follows: the height of doctor blade of 2 ± 0.5 mm, the sliding speed of doctor blade: 60 mm/s, substrate: glass, the temperature of substrate: 25 °C, and the drying speed of solvent was retarded through covering the cast with a perforated lid. The resulting data were summarized in Table S2.

Table S2. Thicknesses of SSPB/IL, SSPB/MMT/IL, SSPB/s-MMT/IL, and Nafion/IL membranes

Membrane	Ionic liquid	Thickness (mm)
SSPB/IL	C2	0.22
	C4	0.24
	C6	0.22
	C8	0.21
SSPB/MMT/IL ^a	C2	0.21
	C4	0.24
	C6	0.25
	C8	0.25
SSPB/s-MMT/IL ^a	C2	0.21
	C4	0.24
	C6	0.22
	C8	0.22
Nafion/IL	C2	0.23
	C4	0.25
	C6	0.24
	C8	0.24

^a The silicate content in the nanocomposites was fixed at 8 wt%.