Supporting Information

1. Materials and Instruments

Materials

3-Sulfopropyl acrylate potassium salt, 1-butyl-3-methylimidazolium chloride, 2hydroxy-2-methylpropiophenone, and methoxyphenol were purchased from Aladdin Reagent Co., Ltd. Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaOH, and NaNO₃ were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Instruments and Methods

The UV-vis absorption spectra of the samples were collected using a UV-Vis spectrophotometer (Shimadzu UV-3600). Scanning electron microscopy (SEM) was performed on a SU8220 microscope. Transmission electron microscopy (TEM) images were acquired on a Hitachi Model H-7650 microscope. Raman spectra was obtained with an in Via Raman Microscope equipment (Renishaw, England) excited by the 532 nm laser. XRD patterns were obtained with a Smart Lab 9 kW X-ray diffractometer (Rigaku, Japan). X-ray photoelectron spectroscopy (XPS) measurements were conducted using the X-ray photoelectron spectrometer (Thermo ESCALAB 250). Differential scanning calorimetry (DSC) was performed on DSC Q2000 in N₂ environment with a scanning speed of 10 °C min⁻¹. The real-time resistance and capacitance were recorded by an Agilent E4980A Precision LCR meter. Digital photographs were taken by a digital camera (CANON 700D). The mechanical tests were conducted on an electronic universal testing machine (SUNS UHM-2102) with a 10 N load cell. The stretching rate was set at 10 mm min⁻¹.

The electrochemical impedance spectra were acquired on an electrochemical station (CHI760E) in the frequency ranging from 0.1 Hz to 1.0 MHz by sandwiching a 0.8 mm thick sample between two copper electrodes. The ionic conductivity of the composites was calculated using the following equation:

$$\sigma = \frac{L}{RA}$$

Whereas L represents the thickness of the sample, R represents the impedance value, and A represents the contact area between the sample and electrodes.

The PIL-LDH composite was cut into strips (20.0 mm \times 3.0 mm \times 0.8 mm) and connected to the LCR meter. The pressure sensor was designed by sandwiching a PIL-LDH (10.0 mm \times 10.0 mm \times 0.8 mm) between two copper electrodes. The obtained sensor was adhered onto the surface of a prosthetic finger to dynamically record the finger movements. For the pressure sensor array, a 10 \times 10 cm² patterned polymer composite film was cut into 5×5 mm² pieces. Patterned copper electrodes were adhered to the PET film (10 \times 10 cm², 25 µm in thickness) with a spacing and a width of 5 mm and 100 mm, respectively. The interdigitated electrode pixels (5 \times 5 mm²) were fixed by crossing the same patterned electrode pixels on the wood substrate of hand orthogonally with PIL-LDH pieces between overlapped area, leading to a large-area and flexible pressure sensor array. The obtained sensor array was attached to a prosthetic hand to measure pressures at different locations.

2. Preparation of the PIL-LDH composites.

Synthesis of the ionic liquid monomer: The ionic liquid monomer was synthesized according to the previous report^[1]. 10 g of 3-sulfopropyl acrylate potassium salt (K[SPA]) salt, 7.51 g of 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and 10 mg of methoxyphenol were mixed in 30 mL of acetonitrile. The mixture was stirred overnight at room temperature then filtered to remove precipitated KCl and evaporated by rotary evaporator to remove solvent to obtain crude product. It was re-dissolve in 50mL of dichloromethane and the solution was kept in refrigerator overnight. After filtration and removal of the solvent, a viscous light-yellow oil-like liquid was obtained ([BMIM]SPA, yield 64%).

Synthesis of the MgAl-SPA-LDHs: Layered double hydroxides (LDH) intercalated with SPA anions were fabricated according to a previously reported procedure^[2]. 9.6 g Mg(NO₃)₂·6H₂O, 4.7g Al(NO₃)₃·9H₂O, and 2.13g NaNO₃ was added in 100 mL H₂O. The pH was adjusted to 10 using NaOH (4 M) followed by aging at room temperature for 12 h. A "wet cake" was obtained after the mixture was filtrated and washed with water until pH close to 7. The sample was then re-dispersed in 130 mL aqueous solution containing 11.605 g K[SPA] salt and the pH was adjusted to 10 using NaOH (4 M). The mixture was aged at 70 °C for 14 h. The resulting precipitation

was filtered and washed with H₂O, and dried in the vacuum oven at 40 °C for 24 h to obtain the final product. In this manner, MgAl-LDH intercalated with SPA anions can be prepared.

Synthesis of PIL-LDH composites: The ionic liquid monomers and LDH powders were mixed with different proportions (for example, 0.1 g LDH in 1 g ionic liquid monomers for the 10% PIL-LDH sample) and vigorously stirred for 3 hours. The suspension was then subjected to sonication for another 6 hours to form a homogeneous and transparent precursor solution. Subsequently, 1 mol% photoinitiator relative to the ionic liquid monomer was added. The precursor solution was sonicated for several minutes to eliminate bubbles and then transferred to a transparent mold and cured under ultraviolet light irradiation (365 nm, 20 μ w cm⁻²) for 20 min to obtain the PIL-LDH composites.



Figure S1. (a) Synthetic route of the ionic liquid monomer and (b) ¹H-NMR spectrum of the ionic liquid monomer. ¹H NMR (400 MHz, D₂O, ppm): 8.68 (s, 1H, H2(imidazole)), 7.45 (s, 1H, H4(imidazole)), 7.40 (s, 1H, H4(imidazole)), 6.42-5.96 (m, 3H, CH₂=CH-), 4.28 (d, 2H, CO-O-CH₂-), 4.17 (t, 2H, N-CH₂-), 3.86 (s, 3H, N-CH₃), 3.07-2.94 (m, 2H, -CH₂-S), 2.18-2.07 (m, 2H, CO-O-CH2-CH2-), 1.89-1.78 (m, 2H, N-CH₂-CH₂-), 1.29 (dd, 2H, N-CH₂-CH₂-CH₂-), 0.90 (t, 3H, N-CH₂-CH₂-CH₂-CH₂-).



Figure S2. PXRD patterns of MgAl-LDHs intercalated with different anions. The interlayer distance was enlarged from 0.7 nm (MgAl-NO₃-LDH) to 1.82 nm (MgAl-SPA-LDH) after the ion exchange process. The PXRD pattern of MgAl-SPA-LDH shows an obvious shift in the (003) Bragg reflection from $2\theta = 11.47^{\circ}$ to 5.88°, indicating interlayer expansion and successful replacement of NO₃⁻ by SPA. The interlayer distance was calculated according to the Bragg's law: $n\lambda = 2d \sin\theta$.



Figure S3. (a) FT-IR spectra of LDHs before and after the ion exchange process. After the ion exchange treatment, the MgAl-SPA-LDH shows characteristic peaks of sulfonate anions (1198 and 1048 cm⁻¹) and acrylate (C=O and C=C at 1724 and 1638 cm⁻¹, respectively) while the peak of the NO₃⁻ anions at 1384 cm⁻¹ disappears. (b) FT-IR spectra of MgAl-SPA-LDH and [BMIM][SPA]. The SO₃⁻ symmetric stretching band shifts from 1040 cm⁻¹ to 1048 cm⁻¹ in MgAl-SPA-LDH, indicating the formation of elastic interactions between SO₃⁻ and positvely charges LDHs.



Figure S4. (a) SEM image of the synthesized MgAl-SPA-LDH. (b) TEM image of ultrathin exfoliated LDH nanosheets after ultrasonic treatment.



Figure S5. Photographs of the dispersed MgAl-SPA-LDH in ionic liquid monomers before and after ultrasonic treatment. The mixture was almost transparent and could exhibit the Tyndall effect, indicating that bulk LDHs were exfoliated into ultrathin nanosheets.



Figure S6. Photograph of the PIL-LDH composites with different shapes (methyl orange was added into the precursor solutions for visual enhancement).



Figure S7. UV-vis absorption spectrum of the pure PIL film.



Figure S8. PXRD patterns of the PIL-LDH composites with different content of LDHs. The results shown here demonstrate that the layered LDHs was exfoliated and dispersed in the polymer matrices.



Figure S9. SEM image and the corresponding EDX elemental mapping of the PIL-LDH composite containing 10 wt% LDH.



Figure S10. Tensile-strain curves of the PIL-LDH composites obtained from successive loading-unloading cycles with increasing strains at room temperature.



Figure S11. Tensile-strain curves of the PIL-LDH composite containing 10 wt% LDH obtained during ten succesive loading-unloading cycles for strains of (a) 100%, (d) 300%, and (c) 500% at room temperature.



Figure S12. Measured fracture toughness of the notched PIL-LDH composites with different LDH contents.



Figure S13. Photographs of the notched PIL and PIL-LDH composite (10 wt% LDH) before and after being stretched to 400%. The PIL-LDH composite shows much smaller extension of notch thus exhibits better tolerance towards break.



Figure S14. Stress-strain curves of the PIL-LDH composite (10 wt% LDH), pure PIL film, and PIL directly mixed with 10 wt% of unexfoliated MgAl-NO₃-LDH.



Figure S15. DSC curves of the PIL-LDH composites containing different contents of exfoliated LDH nanosheets. Glass transition temperatures (T_g) of the PIL-LDH composites were estimated from the temperature of the intersection point of the DSC curve with the bisecting line of the two tangents.



Figure S16. Tensile-strain curves of the PIL-LDH composite containing 10 wt% LDH obtained from two succesive loading-unloading cycles at 100% strain (-65 °C).



Figure S17. Relative resistance changes of the PIL-LDH composite (10 wt% LDH) as a function of the applied strain.



Figure S18. Cyclic stability of the strain sensor at -65 °C (200% Strain).

Content	Tensile	Young's	Elongation-	Toughness	Fracture
	strength	modulus	at-break (%)	(MJ/m ³)	toughness
	(MPa)	(MPa)			(kJ/m ²)
0	0.047	0.029	822	0.22	0.25
5 wt%	0.098	0.035	767	0.37	0.46
10 wt%	0.20	0.050	652	0.60	1.11
15 wt%	0.24	0.056	554	0.65	1.61
20 wt%	0.34	0.079	482	0.73	1.72

Table S1. Summary of the mechanical properties of the PIL-LDH composites with different LDH contents.

Table S2.	Summary	of the a	nti-freezing	performance	of recently	reported	stretchable
ionic cond	luctors.						

Reference	Material	Elongation at low temperature (%)
Chem. Mater. 2020, 32, 2, 874-881	PDESs	320%, -23°C
ACS Appl. Mater. Interfaces 2021, 13, 29008–29020	PVA-IL-H ₂ O hydrogel	244%, -50 311%, -30
Nat. Commun. 2021, 12, 4082.	PAA/zwitterion hydrogel	300, -50°C 100%, -60°C
Adv. Funct. Mater. 2021, 2009438	polySH hydrogel	325%, -40 °C
ACS Appl. Mater. Interfaces 2019, 11, 44, 41710-41716	Cellulose-BzMe ₃ NOH hydrogel	216%, -20 174%, -30 125%, -40 89%, -50
ACS Appl. Mater. Interfaces 2021, 13, 34942–34953	PANI/CS-PAAm DN hydrogel	310%, -40°C
Adv. Funct. Mater. 2021, 2104071	DMAEA-Q/ Fe ³⁺ organohydrogel	100%, -30°C
Adv. Funct. Mater. 2020, 30, 2007291	PAMPS/PAAm organohydrogel	275%, -20°C
Adv. Funct. Mater. 2021, 2105264	PVA-Mexene organohydrogel	220%, -25°C
J. Mater. Chem. A, 2021, 9, 7935– 7945	PVA/CMC/f-BNs organohydrogel	315%, -45°C
J. Mater. Chem. A, 2019, 7, 5949- 5956.	PAAm/PVA/CNT/ PEDOT: PSS organohydrogel	500%, -25°C
Mater. Horiz., 2020, 7, 2994-3004	PIBA-PMEA ionogel	400%, -30°C
ACS Appl. Mater. Interfaces 2020, 12, 33, 37597–37606	P(VDF-co-HFP) ionogel	280, -40°C
This work	PIL-LDH	328%, -75°C

Reference	Material	Conductivity (mS cm ⁻¹)	Temperature range (°C)
Mater. Horiz., 2020, 7, 2994	PIL	0.131	-25~400
Macromolecules 2021, 54, 896	PIL-PEGMA	0.001	9.2~300
Chem. Mater. 2020, 32, 2, 874	PDES	0.4	-23~60
Adv. Funct. Mater. 2021, 31, 2104963	PDES DN elastomer	0.57	-40~60
Adv. Funct. Mater. 2022, 32, 2112293	Fluorinated elastomer/LiTFSI	0.035	-20~300
Nat.Commun. 2018, 9, 2630.	PBA elastomer/LiTFSI	0.063	N.A.~300
Adv. Mater. 2021, 2101396	PEO/LiTFSI	0.204	-40~385
Adv. Mater. 2021, 33, 2006111	PIBA-co-PMEA/ LiTFSI	0.0528	-14.4~200
This work	PIL-LDH	3.3	-81~300

Table S3. Summary of the ionic conductivities and corresponding working temperature

 ranges of recently reported solid-state ionic conductors.

Reference	Material	Antifreezing capability (°C)	Tensile strength (MPa)	Stretchability (%) RT	Ionic conductivity (mS/cm)	Transpare ncy
Chemical Engineering Journal, 2021, 414: 128903.	Lignin- cellulose hydrogel	25	0.216	275	1.2	N
Chemical Engineering Journal 2021,411: 128506	PIL-PAA/PEO	/	0.039	321	0.36	Ν
ACS Appl. Mater. Interfaces 2019, 11, 23, 21117-21125	PAM/PDA/Au organohydrogel	-15	0.053	600	/	Ν
J. Mater. Chem. A, 2019, 7, 5949–5956	PAA/PVA/CNT organohydrogel	-25	0.028	550	/	Ν
ACS Appl. Mater. Interfaces 2021, 13, 4, 5614–5624	PIL-BMIMBF4 ionogel	-75	0.101	604	2	Y
Chem. Mater. 2020, 32, 6310–6317	P(VDF-HFP) ionogel	-25	0.123	580	0.0056	Y
Mater. Horiz., 2020, 7, 2994 -3004	PIL	-25	0.24	540	0.131	Ν
This work	PIL-LDH	-81	0.2	652	3.3	Y

Table S4. Comprehensive comparison of the properties of recently reported stretchable ionic conductors.

Reference	Material	Sensing range	Sensitivity
ACS Appl. Mater. Interfaces 2019, 11, 26412	PAAionogel	0~400	1.29
Adv. Mater. 2020, 2002706	PU ionogel	0~50%, 50~300%	1.23, 1.54
ACS Appl. Mater. Interfaces 2020, 12, 56509.	Ag/CNC/TA-PAAm hydrogel	0~100%	1.02
Adv. Funct. Mater. 2019, 29, 1806220	PVA/HPC hydrogel	0~100%	~0.95
ACS Appl. Mater. Interfaces 2019, 11,3,3506.	PHEMA- AMPS/Clay hydrogel	0~100%	1.8
Adv. Funct. Mater.	PVA/CNF	0~150,	1.2,
2020, 30, 2003430	organohydrogel	150~300%	1.5
J. Mater. Chem. A, 2020, 8, 4447	Gelatin organohydrogel	0~300%	1.5
ACS Appl. Mater.	PAA-PCA	0~200%,	1.128,
Interfaces 2021, 13, 51546	organohydrogel	200~400%	1.486
Adv. Funct. Mater,	PDES/Cellulose	0~300,	1.46,
2022,2202533.	elastomer	300~800%	2.59
Adv. Mater.	PIBA-	0~100%,	1.6
2021, 33, 2006111	PMEA/LiTFSI elastomer	100~200%	4,0
Chem. Mater.	PACMO organogal	0~60%,	1.98,
2019, 31, 3257	r ACINO Organoger	60~110%	2.86
This work	PIL-LDH	0~600%	4.57

Table S5. Summary of the strain sensing ranges and measured gauge factors of rencetly

 reported stretchable ionic conductors.

Supporting References

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- 2 S. Naseem, S. P. Lonkar, A. Leuteritz and F. J. W. J. Labuschagné, *RSC Adv.*, 2018, 8, 29789 -29796.