

**Supporting Information for “Quasi-Solid Electrolyte:
Thixotropic Gel of Imogolite and Ionic Liquid”**

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Methods

Chemicals : Deionized water was further purified using a Milli-Q® Advantage A10® system (Millipore™, Eschborn, Germany), and used throughout the experiments.

Other reagent-grade chemicals except for IG were purchased from Tokyo Kasei Chemicals, Wako Pure Chemical Industries, or Sigma-Aldrich, and used as received.

Imogolite (IG) synthesis^{S1}

Aqueous solutions of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (9.96 g in 369 mL of purified deionized water; Kanto Chem. Co. Inc., Japan) and Na_4SiO_4 (6.90 g in 362 mL of purified deionized water; Junsei Chem. Co. Ltd., Japan) were mixed to prepare a solution containing 12.5 and 2.5 mol L⁻¹ of Al and Si, respectively. The pH of the mixture was adjusted to 6.0 by rapidly adding ~ 26 mL of 1.0 mol L⁻¹ NaOH *aq.* (the solution was stirred vigorously so as to avoid the occurrence of local high pH). The resulting solution was stirred for 1 h. The resultant white precipitates were collected by centrifugation and were redispersed in 400 mL of water under stirring. After adding another 2400 mL of water, the solution pH was adjusted to 4.5 by adding 7 - 8 mL of 1.0 mol L⁻¹ HCl. The solution was then carefully and continuously heated for 4 days at 100 °C under gentle stirring. The as prepared IG solution was then cooled to room temperature and a fine powder of sodium chloride (16.4 g) was added to it under vigorous stirring. The resulting gel was collected

by centrifugation (5000 rpm, 30 min) and was subsequently washed portionwise with 500 mL water using a 100 nm Millipore filter under suction. The wet products (caution should be observed to never let them dry out) were added to 1800 mL of tetrahydrofuran (THF; stabilizer-free grade) under stirring, and the fluffy precipitates were collected by filtration and dried *in vacuo*, resulting in a yield of 42%.

Preparation of the mixture of IG and ionic liquid (IG-IL)

A calculated amount of IG in pure water was sonicated for 4 h at 100 W (FU-21H, SD-Ultra Ltd., Korea) while the room temperature was maintained by occasional addition of ice to the sonicator bath. By this procedure, slightly opaque solutions of 0.2 mol L⁻¹ aluminol functional groups were obtained, and the average length of IG in the solution was shortened to 131 nm, which was confirmed by transmission electron microscopic observation.^{S1} The obtained IG water dispersion was mixed with ionic liquid (IL) such as 1-Butyl-3-methylimidazolium tetrafluoroborate ([BmIm][BF₄]), 1-Ethyl-3-methylimidazolium tetrafluoroborate ([EmIm][BF₄]), 1-ethyl-3-methylimidazolium methanesulfonate ([EmIm][MeSO₃]), and 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BmIm][TFSI]). Then, the mixture was evaporated for 6 h, and dried at 50 °C for 12 h to obtain the IG-IL liquid. The IG-IL solid was prepared from the as prepared IG solution according to same procedure as the

preparation of IG-IL liquid.

Preparation of the mixtures of IG and dicarboxylic acid (IG-DA aq.)^{S2}

A calculated amount of IG in pure water was sonicated for 4 h at 100 W (FU-21H, SD-Ultra Ltd., Korea) while the room temperature was maintained by occasional addition of ice to the sonicator bath. By this procedure, slightly opaque solutions of 0.2 mol L⁻¹ aluminol functional groups were obtained, and the average length of IG in the solution was shortened to 131 nm, which was confirmed by transmission electron microscopic observation.^{S1} To the 0.16 mol L⁻¹ IG aqueous solution (1 equivalent with respect to the -Al(OH)₂ group), the same volume of aqueous solution of dicarboxylic acid (DA) such as maleic acid (MA), fumaric acid (FA), citraconic acid (CTA), and mesaconic acid (MSA), was added with stirring. The mixing ratio was controlled by changing the molar concentration of the latter aqueous solution. The gelation behaviour was observed by the sample tube inversion test at 21 ± 2 °C.

Preparation of the mixture of IG-DA and IL (IG-DA-IL)

To obtain IG-DA-IL, IL was added to the mixture of IG and DA prepared according to procedure shown in the previous section without incubation. Then, the mixture was evaporated for 6 h, and dried at 50 °C for 12 h to obtain the IG-DA-IL.

Transmission electron microscopy (TEM)

TEM observation was performed by using a JEM-2100 (JEOL, Tokyo, Japan) at 200 kV acceleration voltage. A 5 μ L of sample solution was dropped on carbon-coated grids (Oken Shouji Co., Tokyo), of which surface was turned to hydrophilic by glow discharge in a reduced pressure. After 3 min, the sample on the grids was blotted by a filter paper, and then the grid was dried in the ethanol vapor atmosphere. The digital TEM data were obtained using a slow-scan charge-coupled device (CCD) camera (Gatan USC1000, Gatan Inc.) and converted into images with a frame size of 1024 \times 1024 pixels. A cold finger and a cold trap cooled with liquid nitrogen were used to prevent sample contamination by the electron beams.

Estimation of water contents

The water contents of samples were measured by Karl Fischer titration, with a dual channel Karl Fischer moisture measurement system CA-200 (Mitsubishi Chemical Analytech Co., Ltd.).

Estimation of ionic conductivity

The ionic conductivities of all samples were measured using the complex impedance method, with a potentiostat/galvanostat SP-150 (BioLogic) in the frequency range from 100 Hz to 1 MHz in a glove box filled with dry Ar gas.

Viscoelastic measurement

The bulk mechanical response of the IG–DA mixtures was measured with a stress-controlled rheometer (AR-G2, TA Instruments, New Castle, DE). Parallel plates (titanium), 60 mm in diameter, were used for the measurement. The plates were placed in a gap of 400 μm , and the temperature was maintained at r.t. Response of storage modulus G' (red circles) and loss modulus G'' (blue squares) of IG–DA mixture after 1 week aging in strain (ϵ) step change measurements from 100% to 1%, recorded at oscillatory angular frequency of 1 Hz; and in ϵ sweep measurements by changing ϵ upward from 0.1% to 3000% (closed symbols) and downward from 3000% to 0.1% (open symbols). The gel/sol transition was confirmed from the crossover point between the storage modulus (G') and the loss modulus (G''); that is, $G' > G''$ when the sample is in the gel state, and $G' < G''$ when the sample turns to the sol state. When the strain was maintained at 100% and abruptly decreased to 1%, as shown in upper graphs, the magnitudes of G' and G'' of the IG–DA mixture were again inversed within several s after the strain change (This is defined as gel/sol transition time (T_{trans})) due to the sol/gel transition.

Differential scanning calorimetry (DSC)

DSC measurement was performed on a Rigaku Thermo Plus DSC 8230 under nitrogen

flow at 10 °C min⁻¹.

X-ray scattering

The X-ray scattering experiments were performed by using the SPring-8 (Hyogo, Japan) synchrotron orbital radiation beam line at BL45XU, which has a double-crystal diamond monochromator and K-B mirrors held at room temperature. The energy of the X-ray was 12.4 keV (wavelength, $\lambda = 0.10$ nm); the beam size was 0.3×0.2 mm. All SAXS experiments were performed on samples that were introduced into a rectangular stainless steel cell (SUS304; 10 mm width, 40 mm height, and 2 mm thickness). The images of the scattering pattern were obtained at a frame size of 487×172 pixels and a pixel size of 172×172 μm using the X-ray photon counting two-dimensional pixel detector Pilatus 300K-W (Pixel Apparatus for the SLS^{S3}). From the SAXS measurement, the q value was estimated according to equation (1):

$$q = 4\pi \sin(\theta/2) / \lambda \quad (1)$$

where θ is the scattering angle. The scattering intensity $I(\mathbf{q})$ is described as equation

$$(2)^{40}$$

$$I(q) = v_0^2 (\rho_p - \rho_s)^2 f^2 S(q) \quad (2)$$

where ρ_p and ρ_s are the scattering length densities of IG and the solvent, respectively; v_0 is volume of IG; and f is the single-particle form factor.^{S4} Here, $S(q)$, the structure factor, is given by equation (3) in the range of $1/L < q < 1/D$, where C is a constant; L and D are the length and diameter of IG, respectively; and d_f is the mass fractal dimension.^{S4} The second term in equation (3) behaves as q^{-df} , and therefore, the fractal dimension E is defined from the exponent in the relation $I(q) \sim q^{-E}$ at $1/L < q < 1/D$.

$$S(q) = 1 + \frac{C(d_f - 1)\Gamma(d_f - 1)L^E (1 + q^2 L^2)^{1/2}}{(1 + q^2 L^2)^{d_f/2}} \times \frac{qL}{d_f - 1} \sin[(d_f - 1) \arctan(qL)] \quad (3)$$

The exposure time at the designated spot of the sample is 1 sec. The photon flux of the X-ray source was about 2×10^{11} photon s^{-1} mm^{-2} . We confirmed that the denaturalization of IG–DA mixtures did not occur even after continuous synchrotron X-ray irradiation for 10 s. Therefore, we judged that there was little radiation damage in our experiments. The specimen-to-detector distance was 2.0 m. The data were corrected by background scattering from pure water alone. The two-dimensional scattering

patterns were circularly integrated and converted into one-dimensional format (denoted as the scattering curve) by using FIT2D software.

Table S1. The values of polarity, viscosity and hydrophobicity of used solvents and ILs.

solvent	Polarity by Reichardt's scale	Viscosity (mPs)	Hydrophobicity	Propriety of IG dispersion
Water	1.0*	0.89 (25 °C)¶	-	Yes
[BmIm][BF ₄]	0.63†	~ 220 (20 °C)‡	Low	Yes
[EmIm][BF ₄]	0.71‡	41 (25 °C)§	Low	Yes
[EmIm][MeSO ₃]	0.44†	163 (25 °C)#	Low	Yes
[BmIm][TFSI]	0.61†	61 (25 °C)•	High	No
THF	0.207*	0.48 (25 °C)¶	High	No
DMSO	0.44*	1.99 (25 °C)¶	Low	Yes
DMF	0.386*	0.80 (25 °C)¶	Low	Yes

*: ref. [S5], †: ref. [S6], ‡:ref. [S7], ¶:ref.[S8], †:ref.[S9], §:ref[10], #:ref.[11], •:product datasheet

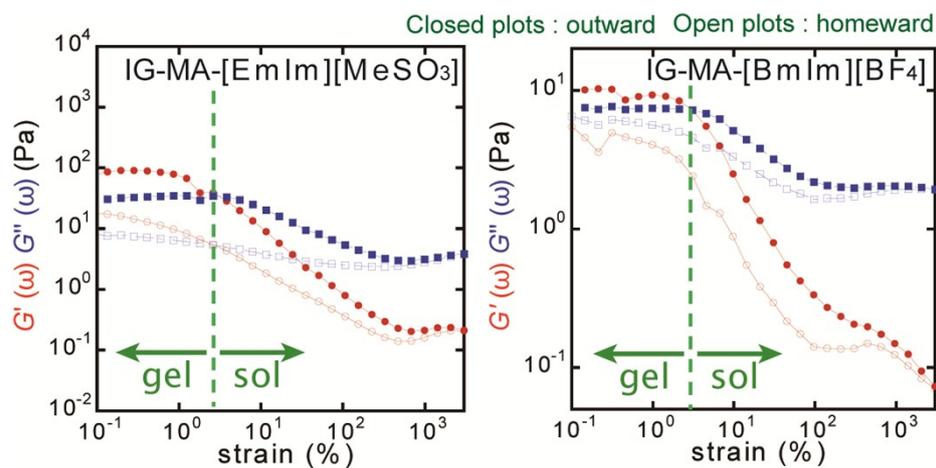


Figure S1. Response of storage modulus G' (red circles) and loss modulus G'' (blue squares) of IG-MA-IL in strain (ϵ) sweep measurements by changing ϵ upward from 0.1% to 3000% (closed symbols) and downward from 3000% to 0.1% (open symbols). $[-\text{Al}(\text{OH})_2 \text{ of IG}] = [\text{MA}] = 0.08 \text{ mol L}^{-1}$. The gel/sol transition was confirmed from the crossover point between the storage modulus (G') and the loss modulus (G''); that is, $G' > G''$ when the sample is in the gel state, and $G' < G''$ when the sample turns to the sol state. In the case of IG-MA-[BmIm][BF₄], the crossover of G' and G'' at downward of ϵ from 3000% to 0.1% cannot be observed until this measurement due to slow transition speed from sol to gel as shown in Figure S3.

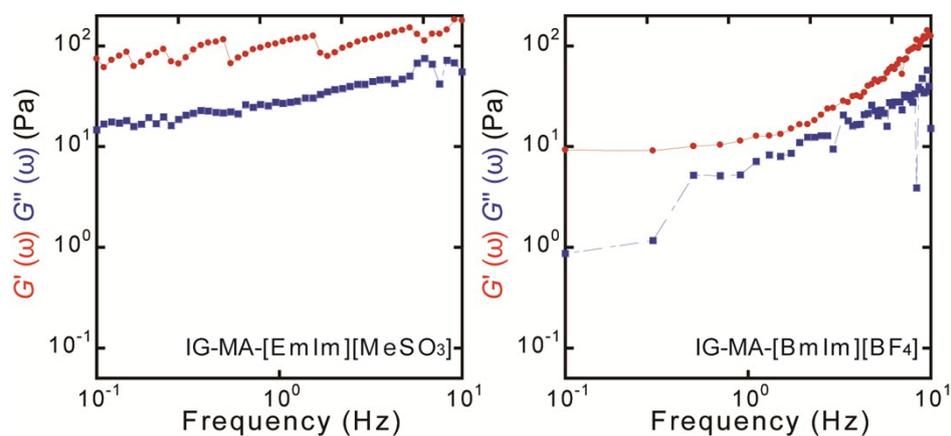


Figure S2. Response of storage modulus G' (red circles) and loss modulus G'' (blue squares) of IG-MA-IL in strain frequency sweep measurements by changing frequency upward from 0.1% to 10 Hz $[-\text{Al}(\text{OH})_2 \text{ of IG}] = [\text{MA}] = 0.08 \text{ mol L}^{-1}$. These bulk mechanical responses of the IG-MA mixtures were measured with a stress-controlled rheometer (AR-G2, TA Instruments, New Castle, DE). Parallel plates (titanium), 60 mm in diameter, were used for the measurement. The plates were placed in a gap of 400 μm , and the temperature was maintained at r.t. In the case of IG-MA-[EmIm][MeSO₃], the G' was not smooth due to some experimental noise such as slip of sample from plates until measurements.

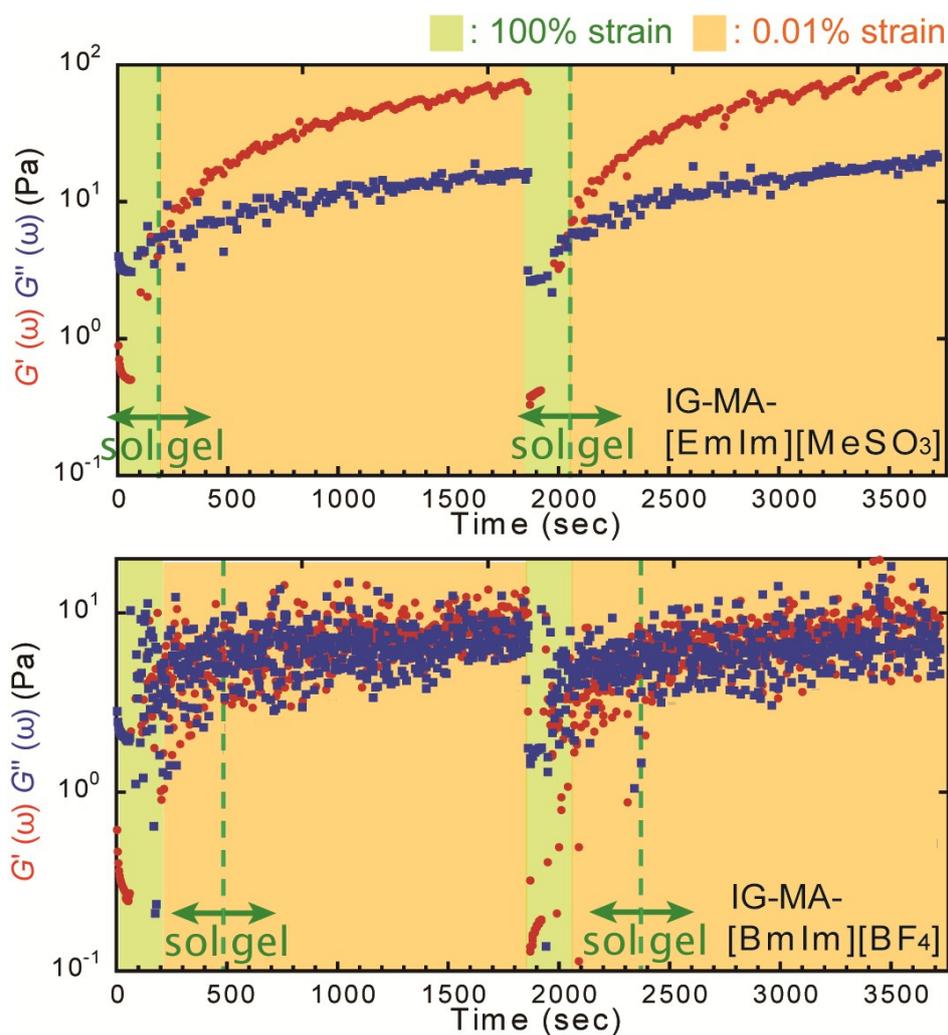


Figure S3. Response of storage modulus G' (red circles) and loss modulus G'' (blue squares) of IG-MA-IL in ε step change measurements from 100% to 0.1%, recorded at oscillatory angular frequency of 1 Hz. $[-\text{Al}(\text{OH})_2 \text{ of IG}] = [\text{MA}] = 0.08 \text{ mol L}^{-1}$. When the strain was maintained at 100% and abruptly decreased to 0.1%, as shown in a, the magnitudes of G' and G'' of the IG-MA-IL were again inverted within several hundred sec after the strain change due to the sol/gel transition. Because the ε sweep measurements of Figure S1 exhibited a crossover point at about $\varepsilon = \text{several}\%$, the gel/sol transition of the IG-MA-IL was induced rapidly at the initial stage of strain increase.

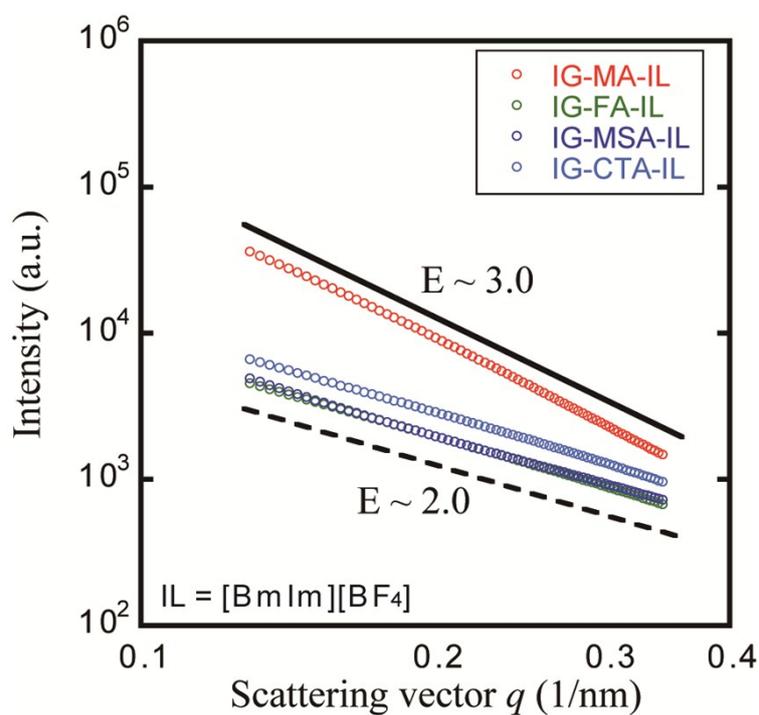


Figure S4. Scattering curves of synchrotron X-ray scattering from IG-DA-IL after 1 week aging ($[-\text{Al}(\text{OH})_2 \text{ of IG}] = [\text{DA}] = 0.08 \text{ mol L}^{-1}$). These measurements were performed with 1 s X-ray irradiation at 59 s intervals. The state of IG substance (*i.e.*, shape of IG aggregate) can be evaluated from the steepness of the X-ray scattering curves (the scattering intensity $I(q)$ versus the scattering vector q) which is described as $I(q) \sim q^{-E}$. Since the region $q = 0.08\text{-}0.3 \text{ nm}^{-1}$ is equal to the real-space size of the IG nanotubes sheathed by MA (131 nm of average length and 3.03 nm of average external diameter^{S1,S2}), E (*i.e.*, fractal dimension of hydrocluster) = 1, 2 and 3 in this region corresponds to the IG nanotubes dispersed separately without forming dense assemblies, those fully packed in a unit space, and those network-like architectures, respectively.

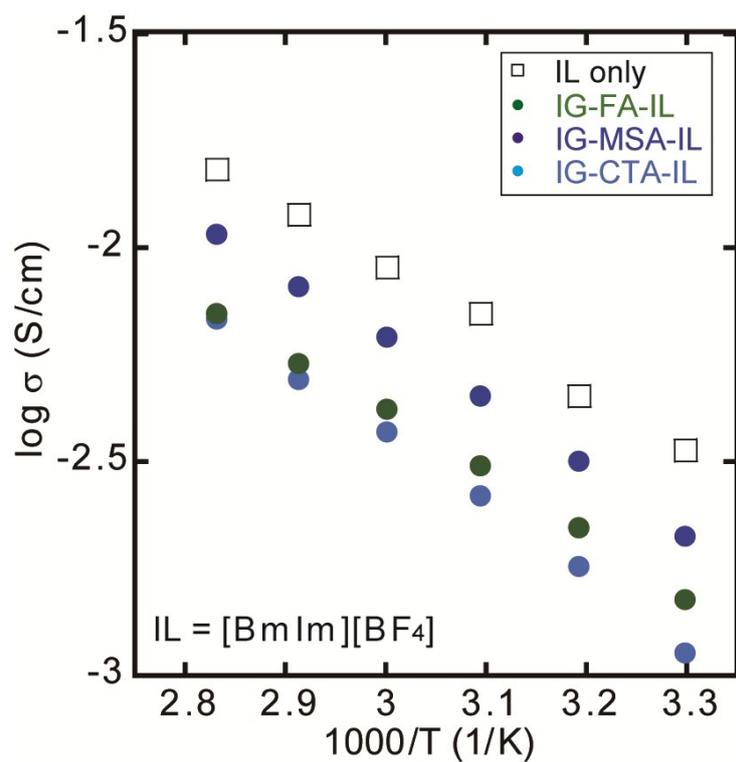


Figure S5. Arrhenius plots of ionic conductivity for IG-DA-IL that showed precipitate of IG and DA.

References

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