Electronic Supplementary Information for

Tough BMIMCl-based ionogels as the integrated electrolyte and separator in high-temperature supercapacitors

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1. Chemicals and materials

BMIMCl was obtained from Lanzhou Institute of Chemical Physics (Chinese Academy of Sciences). Chitosan and HEMA were purchased from Energy Chemical Co. (Shanghai). Activated charcoal powder (YP80F, 2100 m^2/g) was purchased from Kuraray Co. Polytetrafluoroethylene and acetylene black were obtained from Aladdin and Shanghai 3F New Material Co. (Shanghai), respectively.

2. Preparation of BMIMCl-based ionogels

Typically, the CS-BMIMCl solution was prepared by mixing chitosan with BMIMCl at 110 ℃ for 6 h at a mass ratio of 3:80. Then, the previous solution and HEMA were mixed together with a weight ratio of 83:17. At last, the ionogel was obtained by an initiator-free UV light polymerization for 45 min. The employed UV lamp of Maxima ML-3500C (Spectronics Corp, USA) could produce UV light with an intensity of 22.4 mw/cm^2 at 365 nm.

The gel electrolyte films with various thicknesses were obtained as follows:

The precursor was first made on a glass base. After that, the ionogel film can be prepared via UV light polymerization. Since the area of the glass substance is a known value, we can prepare ionogel films with various thicknesses by using different volumes of the precursor. The thinnest ionogel prepared in this work is 100 μm. The ionogel electrolytes with various thicknesses (100-500 μm) were fabricated and tested.

To exhibit temperature-dependent swellability of the ionogel, the swollen volume ratios were obtained at different temperatures. Let set for 3 hours, then the swollen volume ratios of the ionogel were calculated as follows:

$$\text{swollen volume ratio} = V_S/V_0$$

where V_S is the volume of swollen BMIMCl ionogel (at different temperatures) and V_0 is the volume of the BMIMCl ionogel at room temperature.

3. Fabrication of supercapacitors

Porous electrodes of sucapacitors were prepared with activated carbon powder, PTFE binder (60 wt%), and acetylene black with a w/w ratio of 80:10:10 respectively. Then the slurry was coated on the titanium plating stainless steel as collector. Finally, the obtained activated charcoal electrodes (with a mass loading of about 5 mg/cm^2) were dried under vacuum at 120 ℃ for 24 h. The symmetrical supercapacitor has a sandwiched structure of ionogel polymer electrolyte film and two activated charcoal electrodes.

4. Characterization and measurement

4.1. Pre-treatment of SEM samples

The ionogel sample was cut by a blade into small cubes with the size of 5×5×10 mm. After that, the shaped samples were dried by supercritical drying process (Critical Point Dryer CPD, K850, Quorum). After the supercritical drying treatment, scanning electron microscope (Hitachi S-4800, JEOL, Tokyo, Japan) was employed to observe the surface structure of the samples at a voltage of 3 kV.

4.2. Rheological Measurement

All the rheological experiments were measured on a parallel-plate geometry of a Thermo Haake Rheostress RS6000 rheometer (Thermo Scientific, Karlsruhe, Germany), which was used to confirm the mechanical strength of the ionogels. The sample films was 20 mm in diameter and 1 mm in thickness. The frequency amplitude sweeps were performed as a function of angular frequency (at a fixed strain of 1%) at the temperature of 25 °C and 200 °C, respectively. The dynamic time sweep measurement was employed to measure the change of storage modulus and loss modulus along with UV irradiated time (with a fixed frequency of 1 Hz and strain of 1%; intensity of 21.6 mW/cm^2) during the in-situ gelation. The strain amplitude sweep of ionogel was carried out at a fixed frequency of 1 Hz. A procedure was employed with γ changes as 1% -500%-1%-500%-1%-500%-1% to investigate the self-recovery behavior of the ionogel in response to the applied shear forces.

4.3. The TGAs of BCH-GPE and BH-GPE

The thermal stabilities of the BMIMCl/PHEMA-Gel Polymer Electrolyte (BH-GPE) and BMIMCl/CS/PHEMA-Gel Polymer Electrolyte (BCH-GPE) samples were studied via a NETZSCH STA409 PC thermogravimetry analyser. The samples (about 5mg) were placed in hermetically sealed aluminum oxide crucibles and then heated from room temperature to 400 ℃ at a heating rate of 10 ℃/min under nitrogen atmosphere.

4.4. NMR measurement

NMR tests were obtained using a Bruker 400 MHz NMR spectrometer. The internal standard material (1,4-Dioxane) is used to calculate the remaining content of HEMA. In a typical measurement, melted BMIMCl and HEMA were mixed together at a weight ratio of 20:80 get a homogenous solution after vigorous stirring. Each quartz tube, containing 0.1 g of the above solution, was irradiated by the UV light (average 22.4 mw/cm^2 intensity at 365 nm). The reaction time is 0 min, 15 min, 45 min, 60 min, respectively. Then, D-toluene (0.6 ml) was used as the solvent to extract unreacted HEMA from mixture in each quartz tube for 24 h, and the extraction was used for NMR tests.

4.5. Mechanical measurement

The tensile-compressive tester (FR-108B, Farui Co.) was employed to measure the compressive stress-strain properties of ionogels. The size of the cylindrical samples was 13 mm in diameter and 8 mm in thickness. The mechanical measurements were carried out at the strain rate of 1 mm min^{-1}. The repeated 50 times 95 % of compress-recovery curve for BCH gel was tested at a rate of 0.5 mm/min. Penetrative force of the fixing BH-GPE or BCH-GPE with 1 mm thickness was test on the tensile-compressive tester. In the testing process, the upper probe, with tip radius of 1mm, moved down through the ion gel film at the rate of 10 mm/min. Adhesive force between the ionogel and the activated charcoal electrodes was measured on the same machine as follow. A mixture of activated charcoal (80 wt%), PTFE (10 wt%) and acetylene black (10 wt%) was cut into small flakes with the area

of 1cm^2. Then, two flakes were fixed to stainless steel sheets via conductive silver glue. At last, the ionogels of BH-GPE or BCH-GPE with 0.5 mm thickness and 1 cm^2 area was tightly compressed between two activated charcoal flakes via fifty gram force for 30 minutes. Finally, the adhesive forces were measured by the tensile-compressive tester with 1 mm/min stretching rate.

4.6. BET Measurement

The nitrogen adsorption–desorption isotherms of activated charcoal at 77 K was measured by an automatic adsorption instrument (TRISTAR3000, MICROMERITICS). The specific surface areas and average pore diameters were calculated by Brunauer–Emmett–Teller (BET) equation. The pore size distribution was estimated by Barrett–Joyner–Halenda (BJH) method.

4.7. Electrochemical properties of ionogels

The activated charcoal powder was acquired from Kuraray Co. The impedance measurements, cyclic voltammetry, and chronopotentiometry were measured by an Autolab PGSTA302N. The charge-discharge curves were carried out at different current densities at the temperature range of 25 °C~200 °C. Besides, the charge and discharge cycle-lifetime tests were taken respectively at the high temperature of 100 °C and 200 °C.

4.8 Electrochemical properties of ionogels

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As for the impedance measurements, the samples were measured in blocking-type cells where the BH-GPE and BCH-GPE samples were sandwiched structured between two stainless steel electrodes with a PTFE spacer and a circular hole. All the tested samples were placed in a temperature-controlled furnace. The impedance measurements were taken in the temperature range of 25 °C ~200 °C over a frequency from 100 kHz to 10 mHz. The samples were thermally equilibrated at each temperature for 60 minutes before measurements. The bulk resistance of the polymer electrolyte, R_b, can be calculated from the fitting procedure, and correspondingly the conductivity of the gel polymer electrolyte is estimated according to the following equation

$$\sigma = l/(A R_b)$$

where l is the thickness of the semi-solid electrolyte and A is the electrode area.

5. Figures：
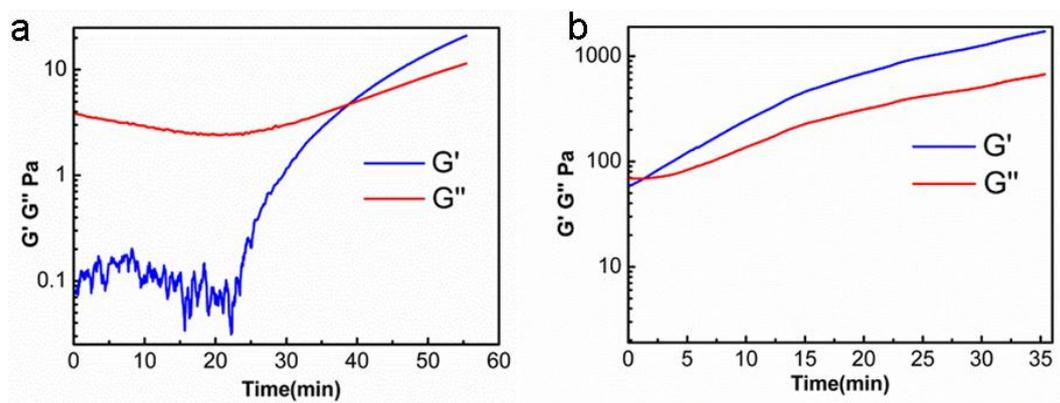
Figure S1. Dynamic time sweeps under UV irradiation. (a) Dynamic time sweep of a gelation system containing 80 wt% BMIMCl and 20 wt% HEMA at a strain of 1% and a frequency of 1 rad s^{-1}. (b) Dynamic time sweep of a gelation system containing 80 wt% BMIMCl, 3 wt% CS, and 17 wt% HEMA at a strain of 1% and a frequency of 1 rad s^{-1}.
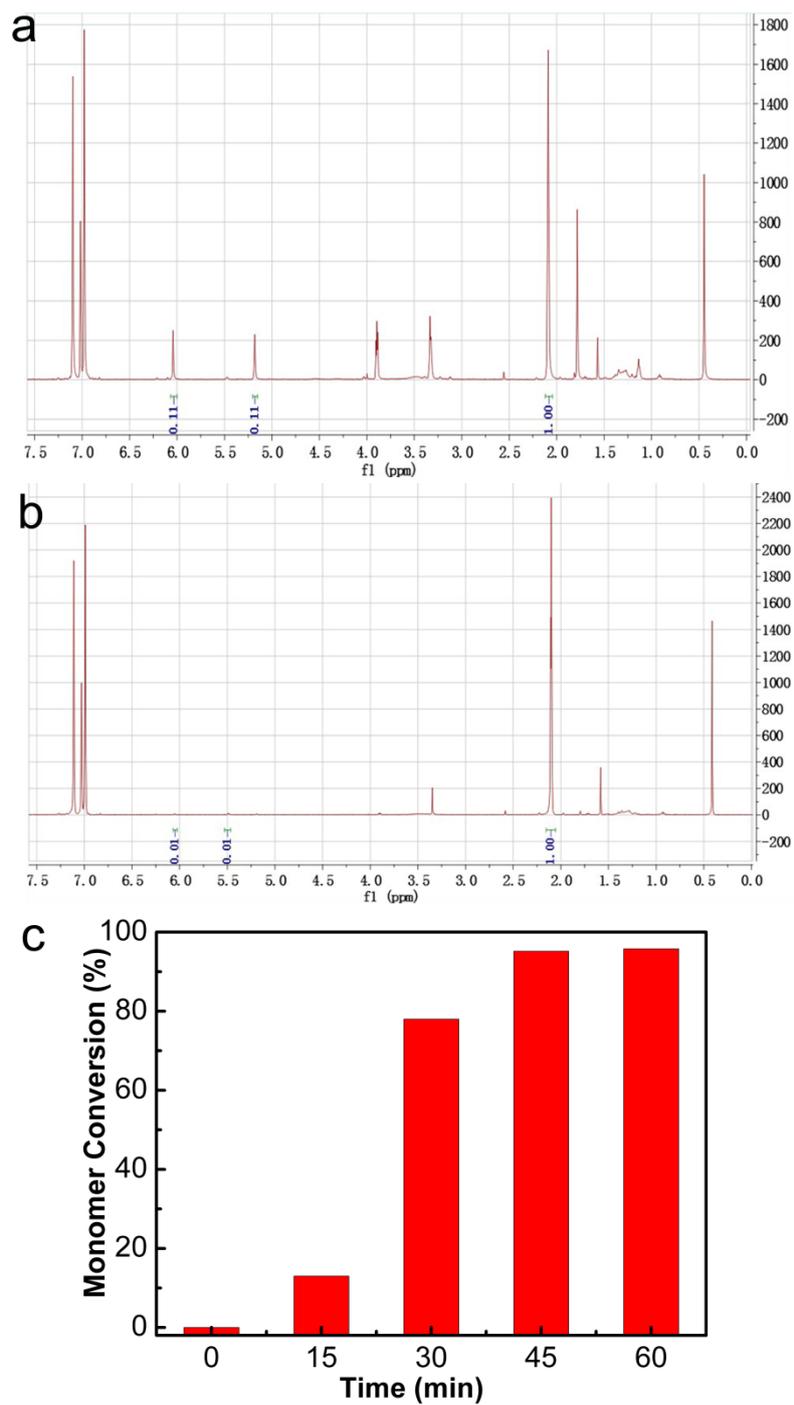
Figure S2. NMR spectra of the precursor containing 20% HEMA and 80% BMIMCl

under different reaction time. (a) 0 min; (b) 60 min; (c) The monomer conversion in

the BMIMCl-based system.
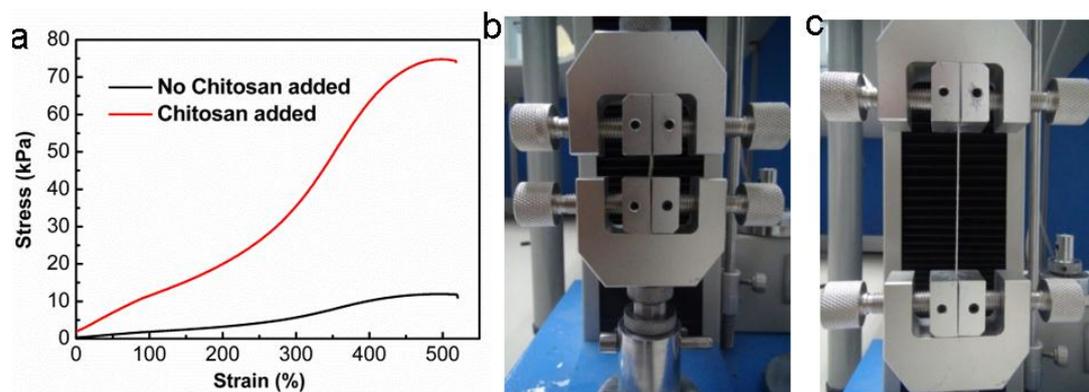
Figure S3. Tensile test of BMIMCl-based ionogels. (a) Tensile results of BH-GPE and BCH-GPE. (b, c) The sequential photographs of the BCH-GPE during the tensile process.
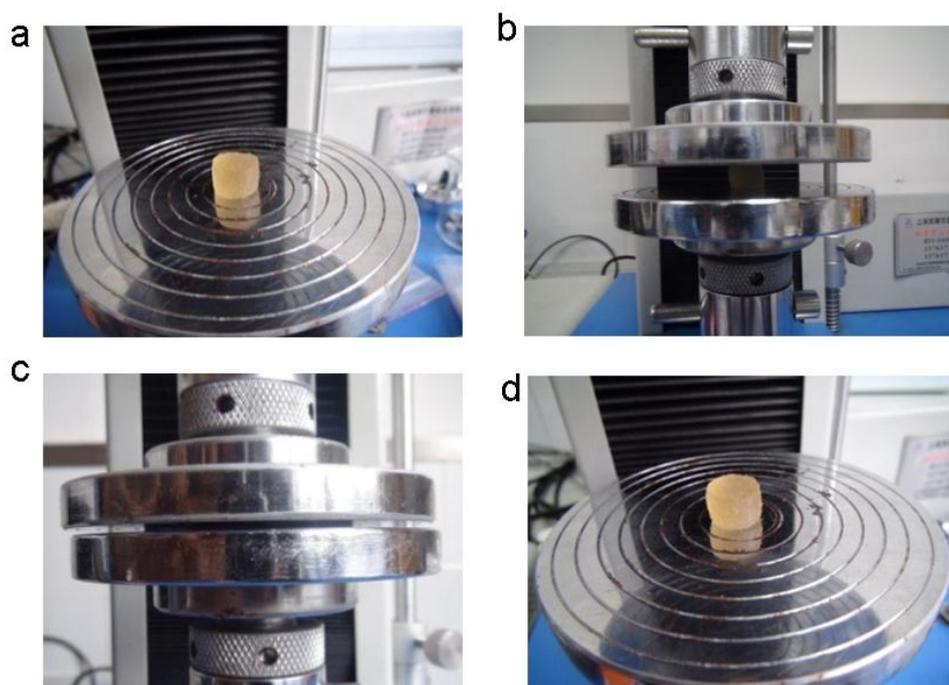
Figure S4. Photographs of the compress-recovery process of BCH-GPE. (a) The intact BCH-GPE before the test. (b) The photograph of BCH-GPE at a strain of 0%. (c) The photograph of BCH-GPE at a strain of 95%. (d) The unbroken BCH-GPE after compress test.
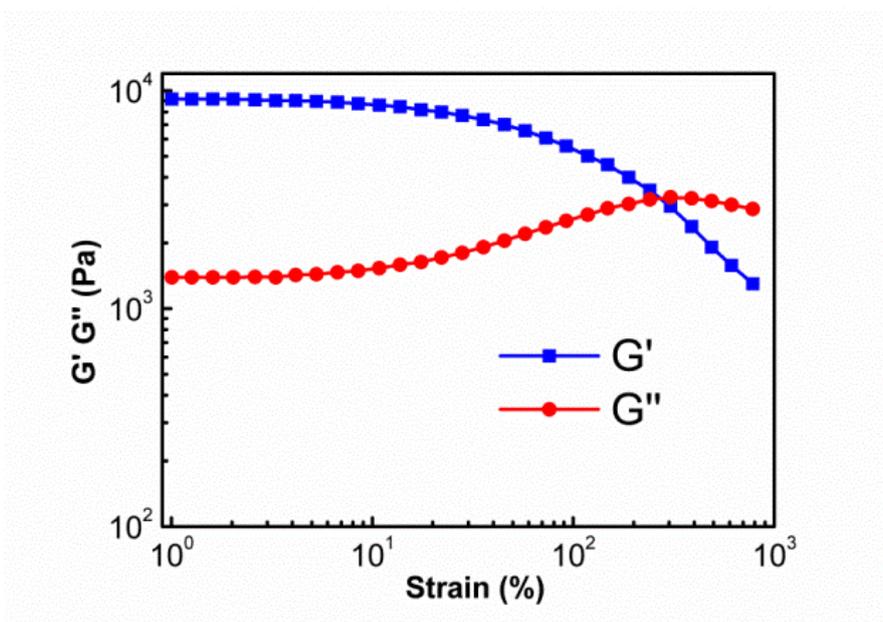
Figure S5. The strain amplitude sweeps of BCH-GPE. Display of a collapse of the gel

state above the critical strain region.
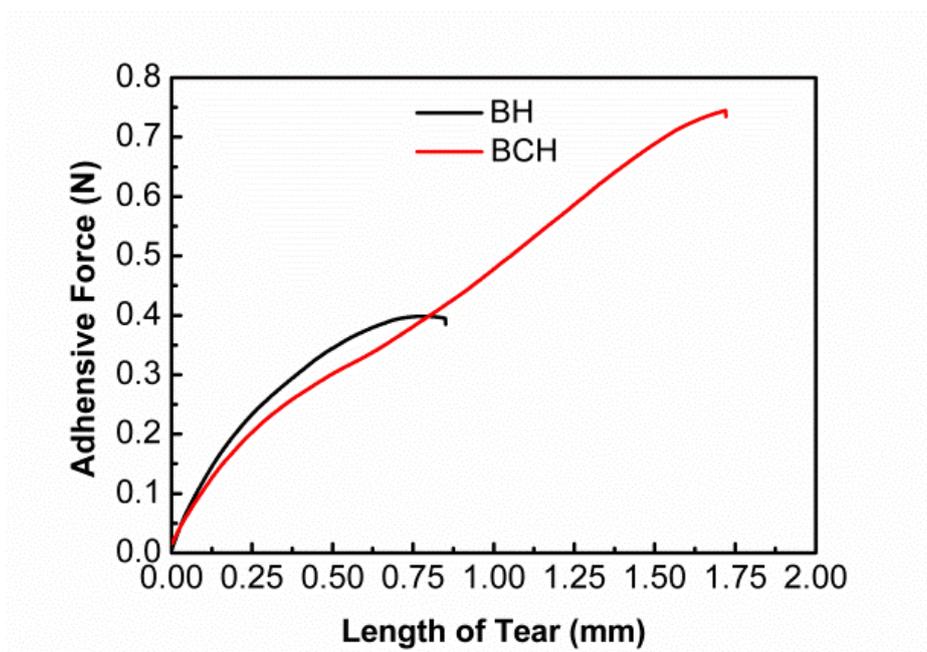
Figure S6. Adhesive forces between the ionogels of BH-GPE or BCH-GPE and the

activated charcoal electrodes with 1 mm/min stretching rate.
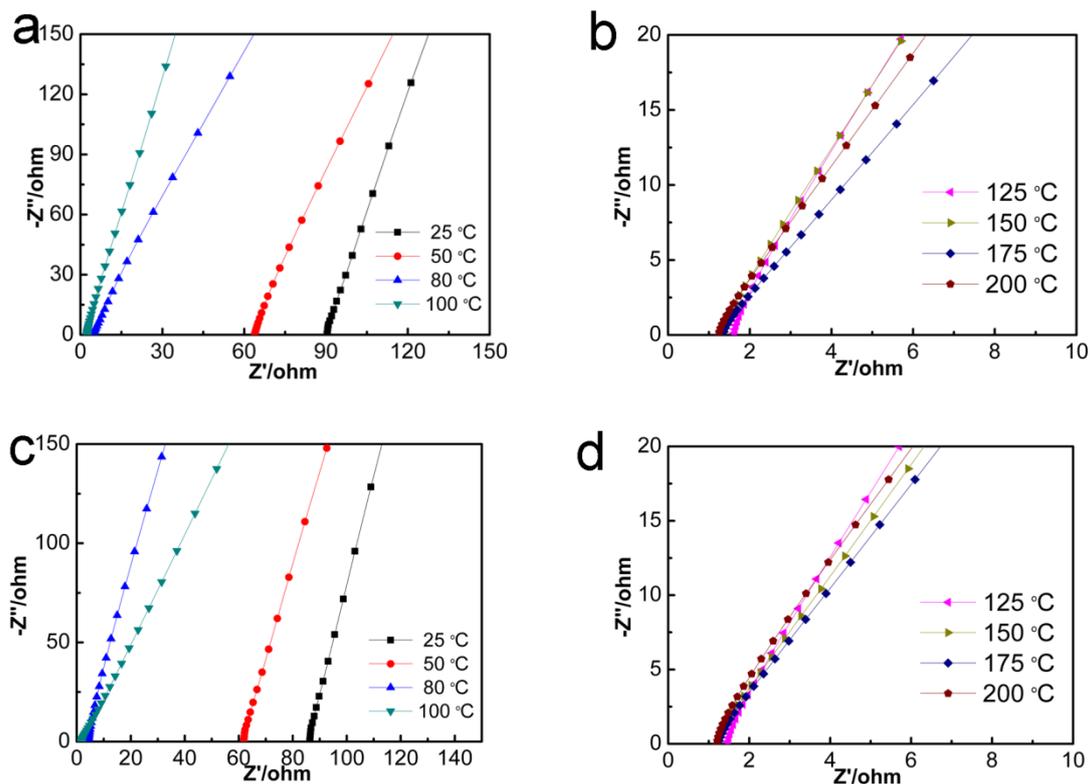
Figure S7. Temperature dependence of the complex impedance spectra for BMIMCl-based gel polymer electrolyte. (a,b) BH-GPE. (c,d) BCH-GPE.
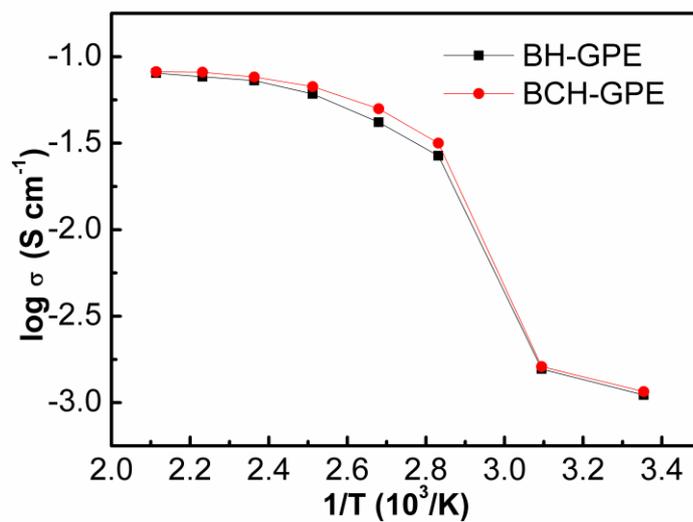
Figure S8. Arrhenius plots of the ionic conductivities of the ionogel polymer electrolytes.
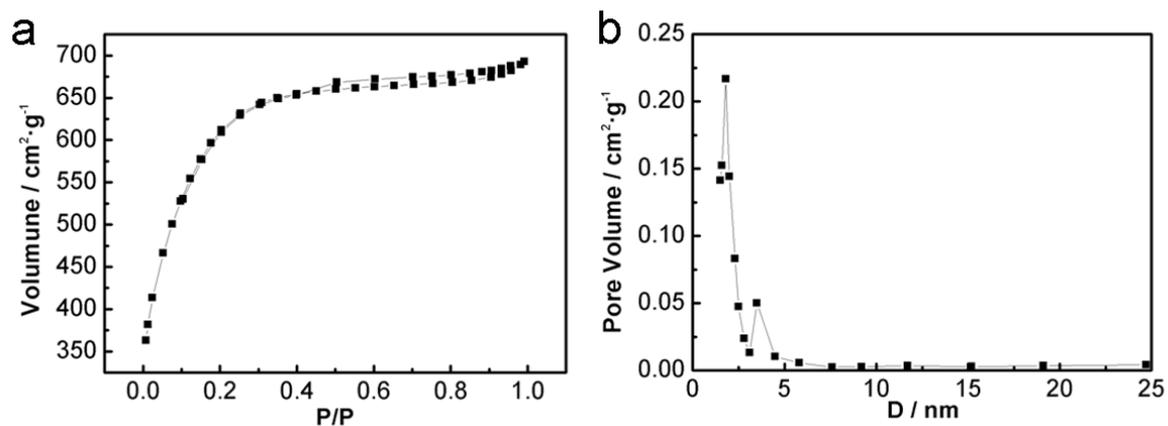
Figure S9. N$_2$ adsorption–desorption isotherms a) and Pore diameters b) of the activated charcoal powder sample.

Table S1

Surface texture properties of activated charcoal.

Sample	S$_{BET}$	S$_{mic}$	S$_{ext}$	S$_{ext}$ /S$_{BET}$	V$_{tot}$	V$_{mic}$	V$_{mic}$/V$_{tot}$	D$_{av}$
	(m^2 g^{-1})	(m^2 g^{-1})	(m^2 g^{-1})	(%)	(cm^3 g^{-1})	(cm^3 g^{-1})	(%)	(nm)
AC	2185	2152	33	1.51	1.071	0.999	93.2	1.96

S$_{BET}$, BET specific surface area; S$_{mic}$, micropore surface area; S$_{ext}$, external surface area; V$_{mic}$, micropore volume; V$_{tot}$, total pore volume; D$_{av}$, average pore diameter.
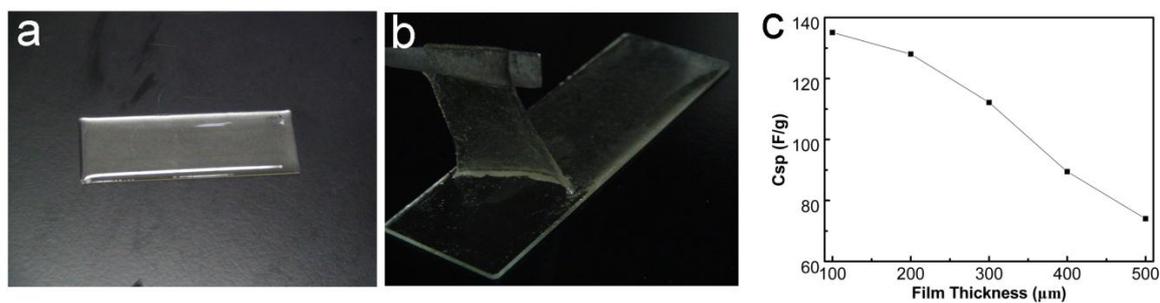
Figure S10. (a) A certain volume precursor was made on a glass base. (b) The ionogel film can be prepared via UV light polymerization. (c) The specific capacitance of the supercapacitors comparing ionogel films with various thicknesses at a current density of 0.5 A/g.
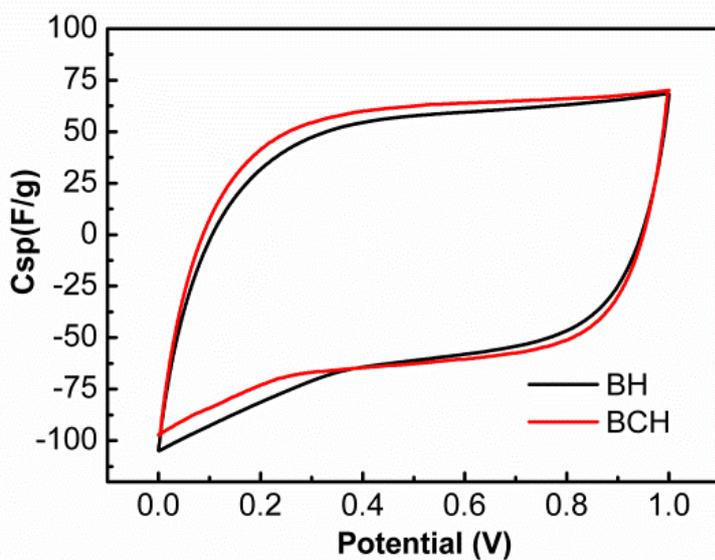
Figure S11. Cyclic voltammetry behaviours of BCH-GPE and BH-GPE based supercapacitors at 80 °C and 10 mV/s.
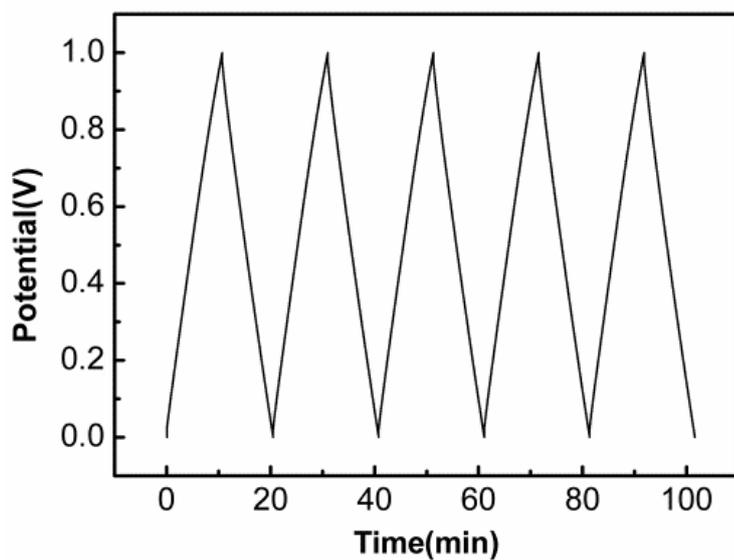
Figure S12. The capacitive behavior of charge-discharge curves at the current of

1mA at 80 °C.
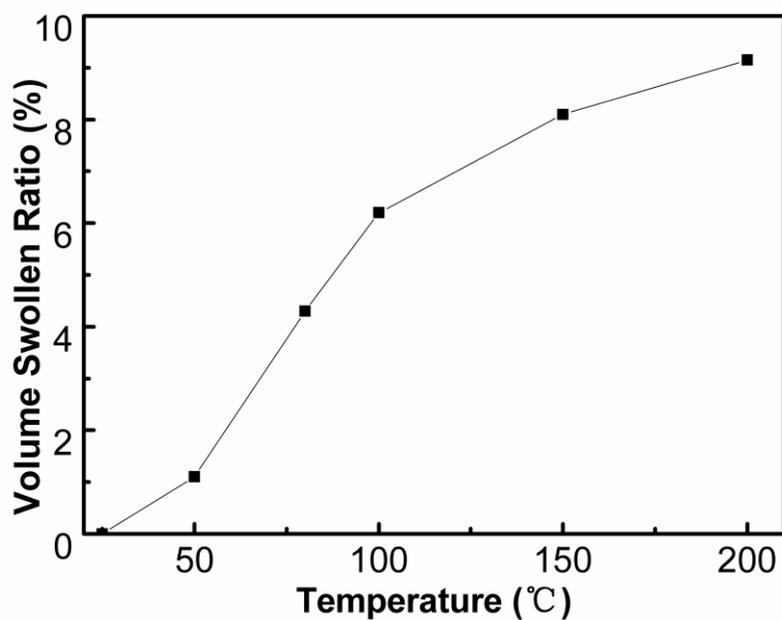
Figure S13. The swollen volume ratios of the BMIMCl based ionogel at high

temperatures relative to the one at room temperature.
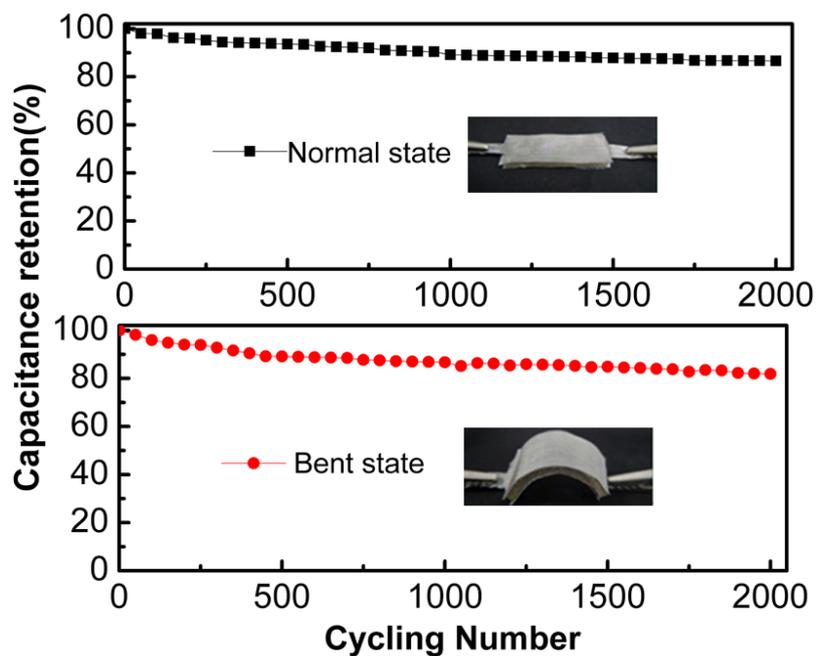
Figure S14. The operation stability of ionogel-based supercapacitors at 100 °C and 0.5 A/g in normal and bent states.
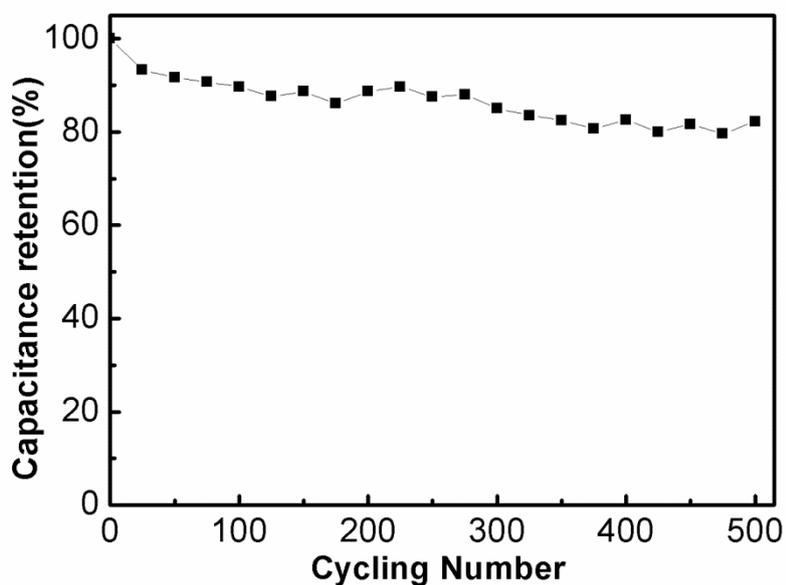
Figure S15. The charge and discharge cycle-lifetime test for 500 cycles at 2.5 A/g and 200 °C.