

Supporting Information

Robust organohydrogel with flexibility and conductivity across freezing and boiling temperature of water

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Experimental section

Materials

2-Acrylamido-2-methylpropanesulfonic acid (AMPS, 99%) and acrylamide (AAm, 98%) were purchased from Energy Chemical Co. Ltd. and recrystallized from methanol and chloroform, respectively. Lithium chloride monohydrate ($\geq 97.0\%$) and ethylene glycol ($\geq 99.0\%$) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used as received. Ammonium persulfate (APS, 98%) and N,N'-methylenebisacrylamide (MBAA, 97%) were purchased from Acros and Alfa-Aesar, respectively. N,N,N',N'-Tetramethylethylenediamine (TEMED, 99%) and 2-oxoglutaric acid (98%) were supplied by Energy Chemical Co. Ltd.. All other reagents were purchased from commercial sources and used as received.

Preparation of HGel

Typically, AMPS (1.036 g), MBAA (30.833 mg) and APS (18.256 mg) were dissolved completely in 5 mL deionized water. Then, TEMED (7 μL) was added into the above solution in an ice bath. After purged with nitrogen for 5 min to remove the dissolved oxygen, the mixture was reacted at 60 °C for 2 h and then continued at room temperature overnight. Subsequently, the PAMPS gels were immersed into the aqueous mixture of AAm (2 M), 2-oxoglutaric acid (2 mM) and MBAA (2 mM) for a certain time until the swelling equilibrium. After irradiated with UV light (365 nm) for 3 h and then immersed in deionized water for 2 days to remove unreacted monomers and other impurities, the final PAMPS/PAAm hydrogel (referred as HGel) were obtained.

Preparation of OHGel

Typically, PAMPS/PAAm hydrogel (about 3 g) were immersed in 30 mL pure ethylene glycol solution or ethylene glycol solution of lithium chloride at different concentrations (1 M, 2 M, 4 M, 8 M), respectively, until the weights of organohydrogels remained stable. The organohydrogels are referred as OHGel- x , where x is the abbreviated LiCl concentration of x mol L⁻¹.

Characterization

Differential scanning calorimeter (DSC)

The thermal analysis of the organohydrogels from -130 °C to 33 °C were performed on a Netzsch 200 F3 differential scanning calorimeter. The heating and cooling rates were 5 °C min⁻¹.

The thermal analyses of hydrogel and organohydrogels from 25 °C to 250 °C were performed on a Netzsch STA 449F5 DSC. The heating rate was 10 °C min⁻¹.

Thermogravimetric analysis (TGA)

The thermogravimetric analyses of hydrogel and organohydrogels were performed on a TA Q500 thermogravimeter. The heating rate was 10 °C min⁻¹.

Rheological characterization measurements

The rheological property of organohydrogels and viscosity of EG/LiCl solution were tested by a rheometer (Anton Paar, 302, GmbH). The organohydrogels were prepared as thick sheets approximately 1 mm to determine the linear viscoelastic region using a frequency sweep mode.

The evolution of storage (G') and loss (G'') moduli were given at 1.0% strain amplitude. The test temperature was 25 °C. The heating rate of rheological property of HGel and OHGel-8 (0 ~ 150 °C) were 2 °C min⁻¹.

Characterization of the mechanical properties

The compressive mechanical properties of organohydrogels were determined by an MTS Insight tensile-compressive test device (MTS Insight Electromechanical Testing System) at a compressive strain rate of 10 % min⁻¹. Each cylindrical test sample was with a diameter of 10 mm and a height of 20 mm. The in-situ tensile strength measurements of hydrogel and organohydrogels were performed on an INSTRON 5966 tensile-compressive test device at -70 °C, 25 °C and 120 °C, respectively. The strain rate was 250 mm min⁻¹.

Characterization of the anti-freezing and anti-drying properties

The anti-freezing properties of organohydrogels were assessed through deformation by hands after stored in a refrigerator at -80 °C for 3 h. The anti-drying properties of organohydrogels were assessed on the weight loss after stored at an oven (120 °C, 10% humidity) or vacuum oven (25 °C), respectively.

Ion conductivity measurements

A round-shape disk HGels and OHGels-8 (diameter of 15 mm) were tested by using electrochemical impedance spectroscopy measurements of CHI 660E, ChenHua Instruments. The tested ac potential amplitude was 0.5 V and the ionic conductivity (σ) is calculated from formula (1).

$$\sigma = \frac{L}{RS} \tag{1}$$

where L represents the thickness, S is area of the film, and R is the resistance.

Table S1. Progress on working temperature of hydrogels or organohydrogels.

No.	Gel network	Key conditions	T _{min} (°C)	T _{max} (°C)	References
1	PAMPS/PAAm	ethylene glycol/LiCl	-80 °C	120 °C	This work
2	Polyacrylamide/alginate	CaCl ₂	-57 °C	Not mentioned	<i>Adv. Mater.</i> , 2018, 30, 1801541.
3	polyacrylamide	LiCl	-80 °C	25 °C (10% humidity)	<i>Appl. Phys. Lett.</i> , 2014, 105, 151903.
4	cellulose	ZnCl ₂ /CaCl ₂	-70 °C	25 °C	<i>Angew. Chem., Int. Ed.</i> , 2019, DOI: 10.1002/anie.201902578.
5	Ca-alginate/polyacrylamide	glycerol, ethylene glycol or sorbitol	-70 °C	20 °C (50% humidity)	<i>Angew. Chem., Int. Ed.</i> , 2018, 130, 6678-6681.
6	HPN/OPN heteronetworks	heptane	-78 °C	80 °C	<i>Nat. Commun.</i> , 2017, 8, 15911.
7	(PAM-co-PAA) networks with (PDA-CNTs)	glycerol	-20 °C	60 °C	<i>Adv. Funct. Mater.</i> , 2018, 28, 1704195.
8	PVA polymer powders and poly(3,4-ethylenedioxythiophene): polystyrene sulfonate	ethylene glycol	-55 °C	45 °C	<i>Angew. Chem., Int. Ed.</i> , 2017, 129, 14347-14351.

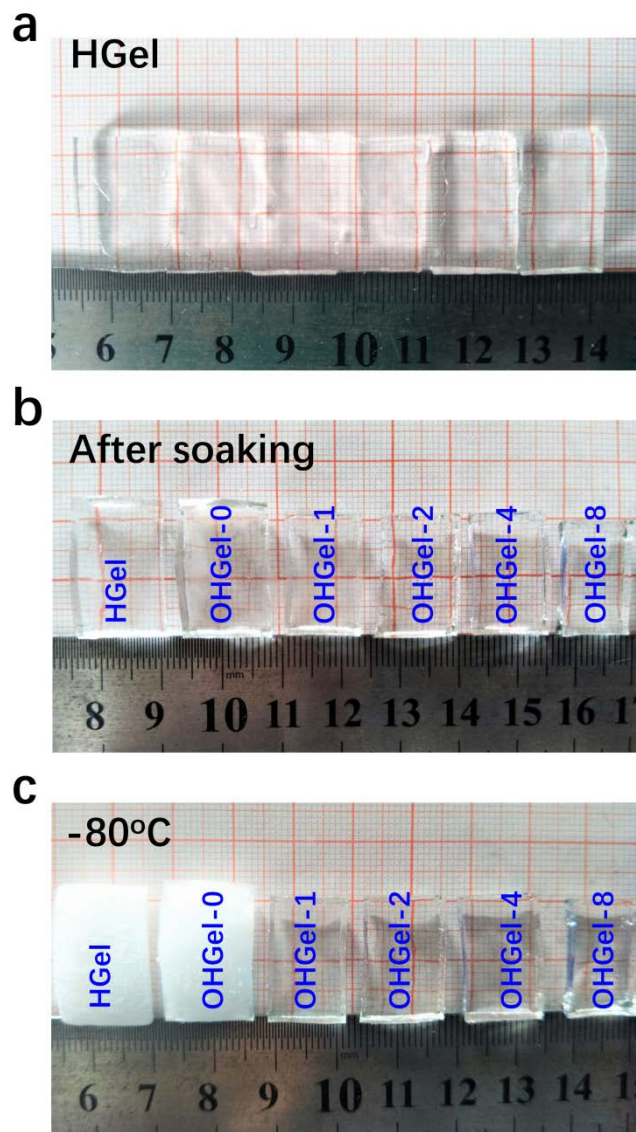


Figure S1. Photos of (a) PAMPS/PAAm hydrogels, (b) organohydrogels after soaking in EG/LiCl for 7 days and (c) stored at $-80\text{ }^{\circ}\text{C}$ for 3 h.

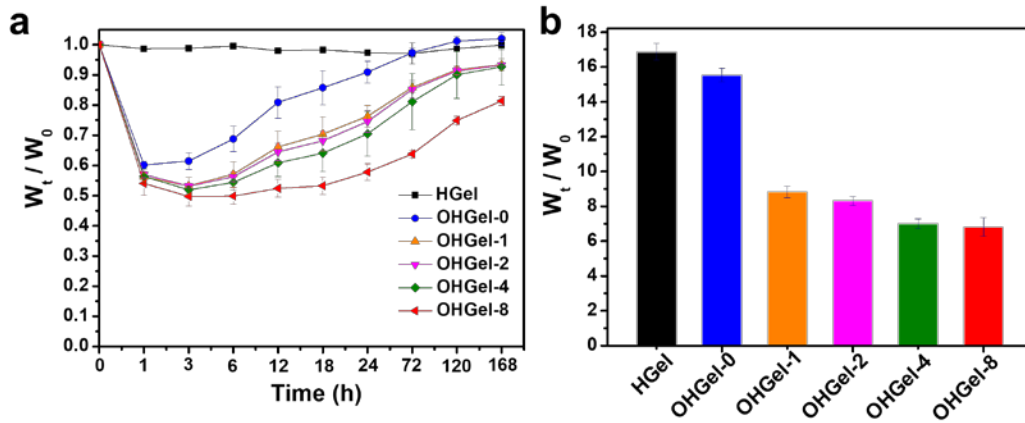


Figure S2. (a) Weight change of pristine hydrogel as a function of time during soaking in different EG/LiCl solutions. (b) Swelling ratios of hydrogel and organohydrogels after immersing a lyophilized hydrogel in water or different EG/LiCl solutions until equilibrium.

The weights of hydrogel and organohydrogels were measured after the surface solvent on gel was removed with filter paper. The swelling method took a longer time (e. g. about one month for OHGel-8) to reach the equilibrium to obtain anti-freezing organohydrogels than the solvent displacement method.

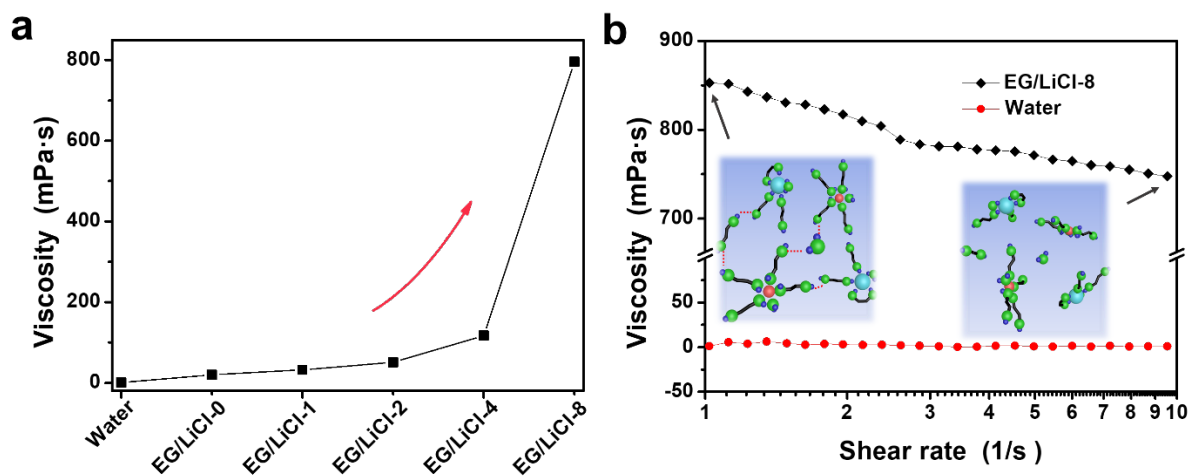


Figure S3. (a) Viscosity of water and EG/LiCl solution. (b) Viscosity of EG/LiCl-8 solution as a function of shear rate (Inserted image shows the interaction between solvent molecules).

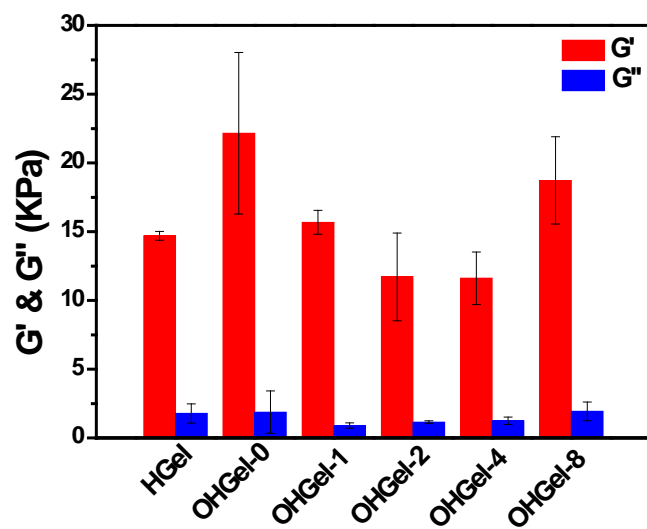


Figure S4. G' and G'' of hydrogels and organohydrogels ($\gamma = 1.0 \%$, $\omega = 50 \text{ rad/s}$, $25 \text{ }^\circ\text{C}$).

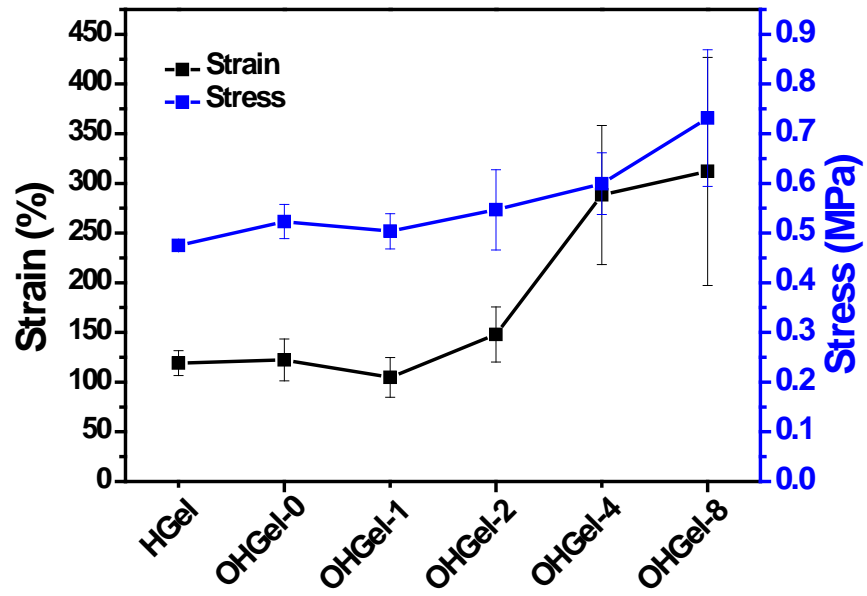


Figure S5. Tensile mechanical properties of the hydrogel and organohydrogels (25 °C).

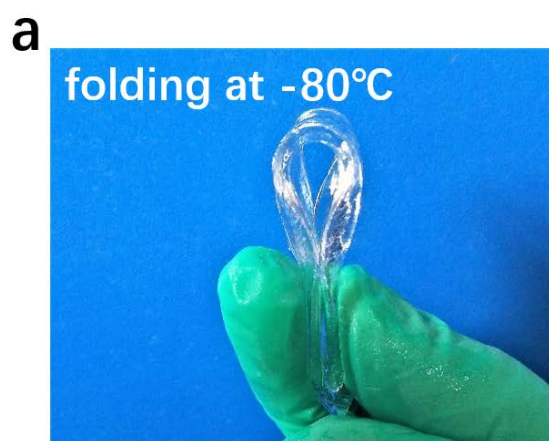


Figure S6. Photos of OHGel-8 after (a) folding and (b) twisting at -80°C .

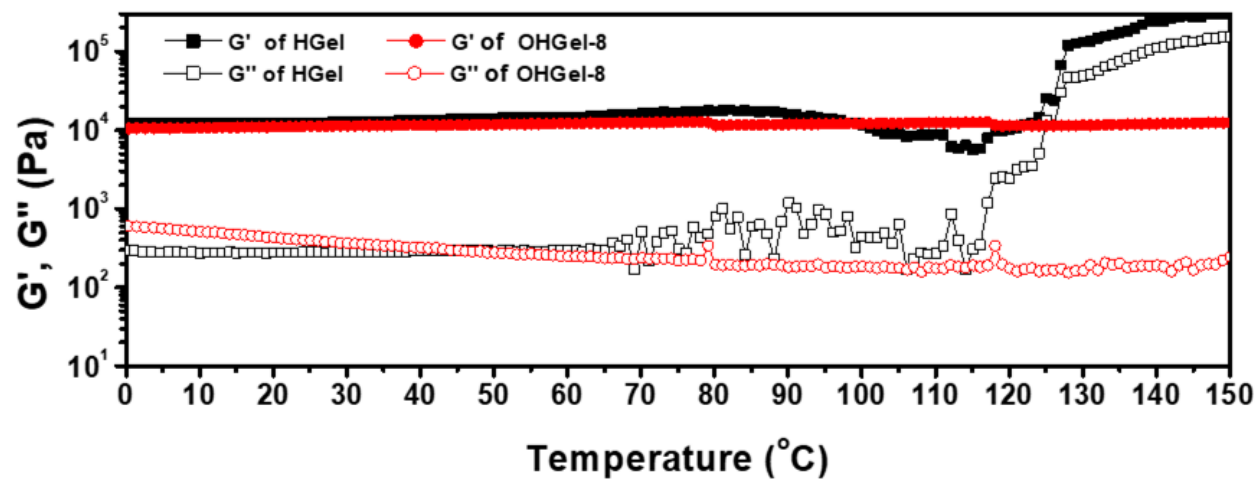


Figure S7. G' and G'' of HGel and OHGel-8 at temperature from 0 °C to 150 °C.

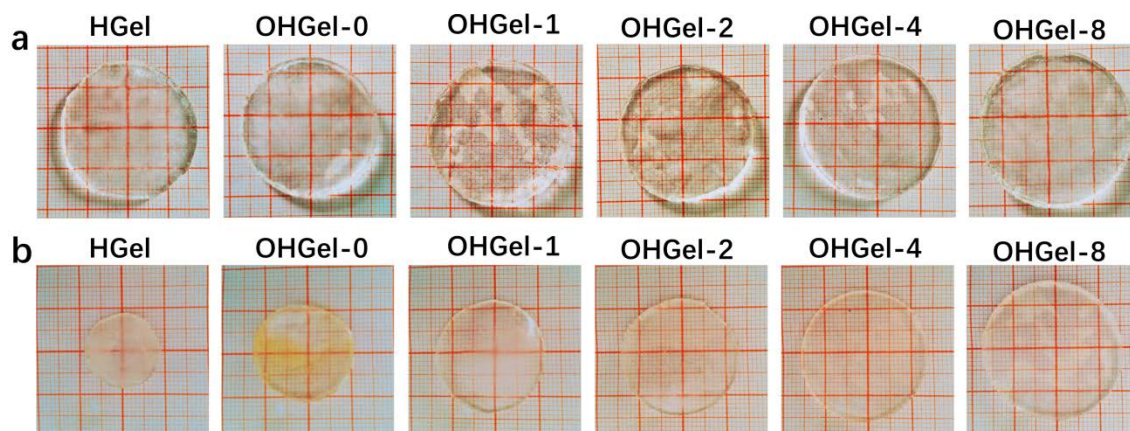


Figure S8. Photos of HGel and OHGels (a) as-prepared and (b) after heating at 120 °C and 10% humidity for 3 h.

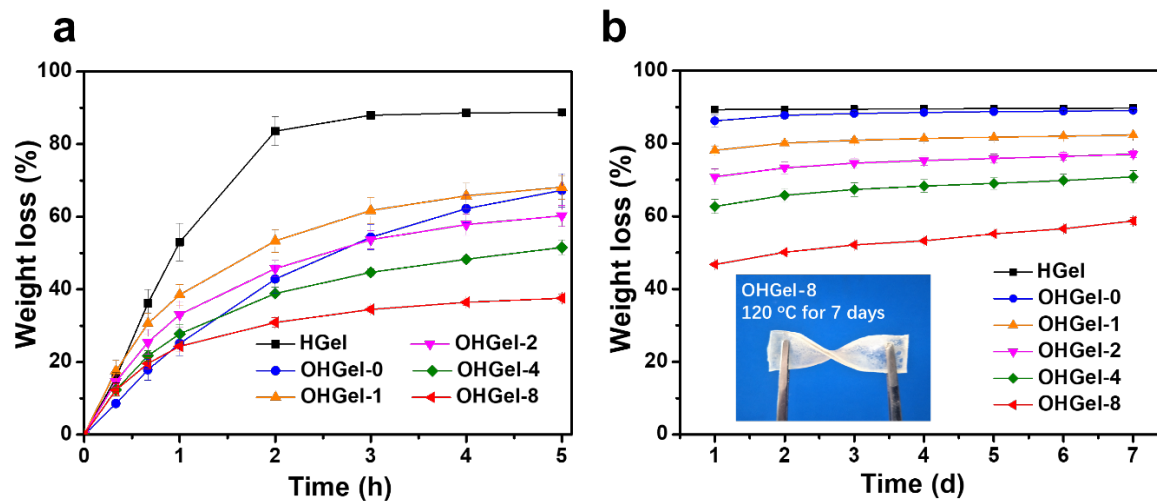


Figure S9. Anti-drying properties of the organohydrogels. Weight loss of organohydrogels as a function of time during drying at 120 °C and 10% humidity (a) in the beginning 5 h, and (b) during the 7 days incubation. Inset: flexibility of OHGel-8 after heating at 120 °C and 10% humidity for 7 days.

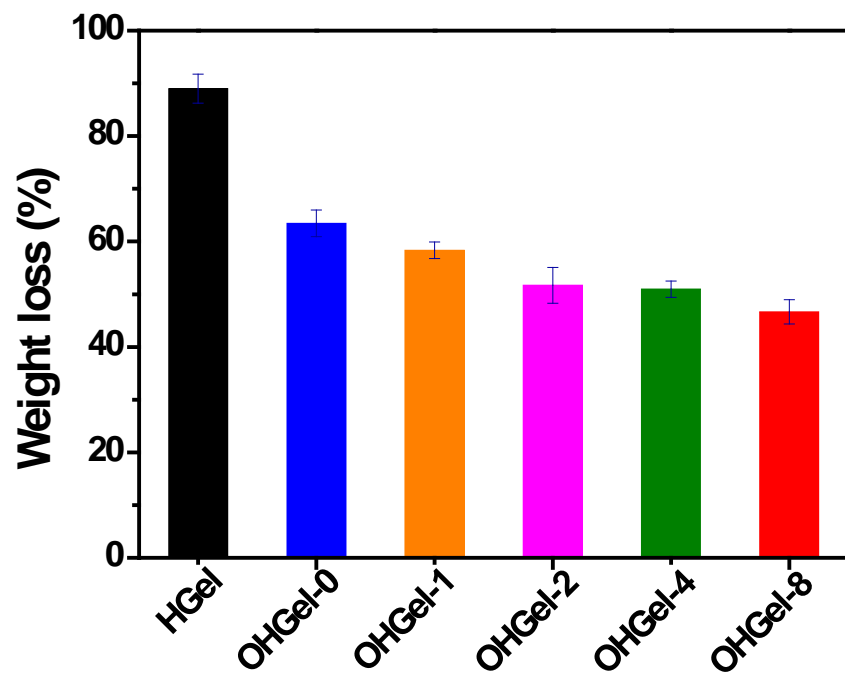


Figure S10. Weight loss of hydrogel and organohydrogels after drying in vacuum for 24 h.

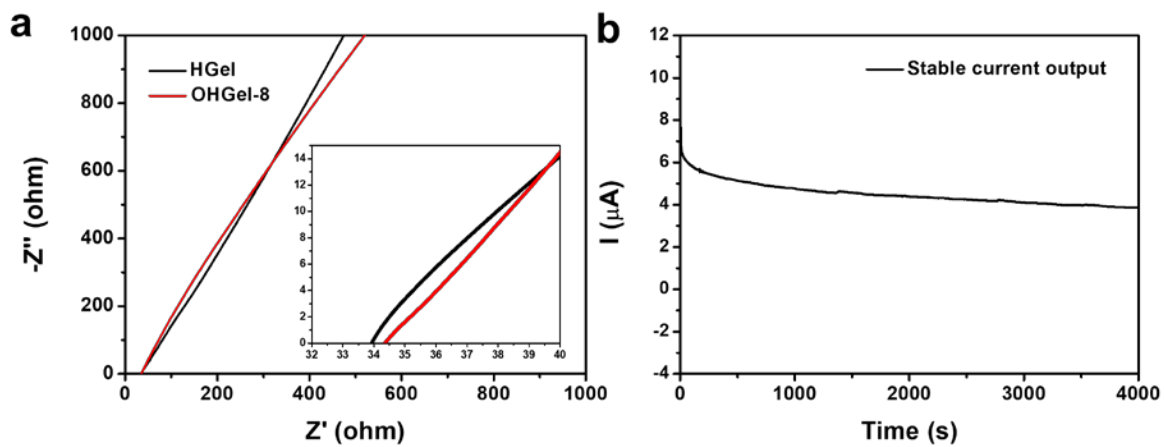


Figure S11. (a) Typical “Nyquist” plot of HGel and OHGel-8 at 25 °C. (b) The stability of ionic conductivity of OHGel-8.

Table S2. Ionic conductivity of HGel, OHGel-0 and OHGel-8 after incubation at $-20\text{ }^{\circ}\text{C}$, $25\text{ }^{\circ}\text{C}$ and $120\text{ }^{\circ}\text{C}$ for 3 h, respectively.

Temperature	HGel	OHGel-0	OHGel-8
$-20\text{ }^{\circ}\text{C}$	N.D. ^a	N.D.	0.071S m^{-1}
$25\text{ }^{\circ}\text{C}$	0.51S m^{-1}	N.D.	0.51S m^{-1}
$120\text{ }^{\circ}\text{C}$	N.D.	N.D.	7.7S m^{-1}

^aN.D. refers to that the conductivity is too low to be detected.