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Supporting Information

Hydrogen bond regulating in hydrogel electrolytes for enhancing the antifreeze ability of flexible zinc-ion hybrid supercapacitor

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Materials

PVA (average polymerization degree: 1700±50, alcoholysis: ≥88%) was purchased from Greagent, cellulose nanofibrils (CNFs, by crushing cellulose paperboard with grinder). TEMPO (2,2,6,6-tetramethylpiperidinooxy) and dimethyl sulfoxide (DMSO, purity: 99.7%) was purchased from Adamas. $ZnSO_4 \cdot 7H_2O$ was purchased from Aladdin Chemical Reagent Co. Raw AC material was purchased from Kuraray (Shanghai) Co., Ltd. Zinc metal foil (0.08 mm) was supplied by Hebei

Tengfeng Metal Material Co., Ltd. China. Carbon back was produced by Sinopharm Chemical Reagent Co., Ltd.

Characterizations

The tensile properties of hydrogel were studied by a universal tensile testing machine (INSTRON, model 5943, 1 kN, America) at 25 °C with a stretching speed of 50 mm min^{-1}. The Fourier transform infrared spectroscopy (FTIR) test was performed on Nicolet-Nexus 670 spectrophotometer at room temperature. The dried gels were triturated with KBr in the radio of 1:100. The samples were ground into powder to analyze their XRD patterns using a Bruker-D8 Advance diffractometer. The hydrogel was shaped into a cylinder with a bottom circle diameter of 1 mm and a height of 30 mm, and the morphologies and structures and the energy-dispersive X-ray spectrum (EDS) of the samples were observed using a scanning electron microscope (SEM, Hitachi S-4800, Japan). The surface composition of the hydrogel was estimated by X-ray photoelectron spectroscopy (XPS, AXIS SUPEA, Kratos Corp) by studying the C 1s, C 2s, O 1s peaks. Nonmonochromatic Al Kα radiation was used and created by a power of 220 W at a pressure of ca. 10^{-7} Pa in the chamber.

Electrochemical measurements

AC cathode was prepared by mixing 80 wt% AC, 10 wt% carbon black and 10 wt% PVDF in an NMP solvent, and then the mixture was coated onto graphite paper, which was dried at 60 °C in constant temperature oven. Typically, each working electrode comprises an exposed area of 1 × 2 cm^2 with a mass loading of 5 mg. Zn metal foil was directly used as anode, which should be polished with finegrained sandpaper to avoid being oxidized. AC//PVA/CNF/DMSO (PCD)-Zn hydrogel//Zn

FZHSC was assembled with PCD hydrogel electrolyte, which also acted as a separator of cathode and anode. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) tests were applied to evaluate the electrochemical behaviors of FZHSCs using an electrochemical workstation (Autolab PGSTAT302N). Electrochemical impedance spectroscopy (EIS) was tested at the electrochemical workstation (Autolab PGSTAT302N). The cycling stability measurement of FZHSC was carried out on a LAND battery-testing instrument with a sweep charge and discharge rate at 3 A g^{-1} for 5000 cycles.

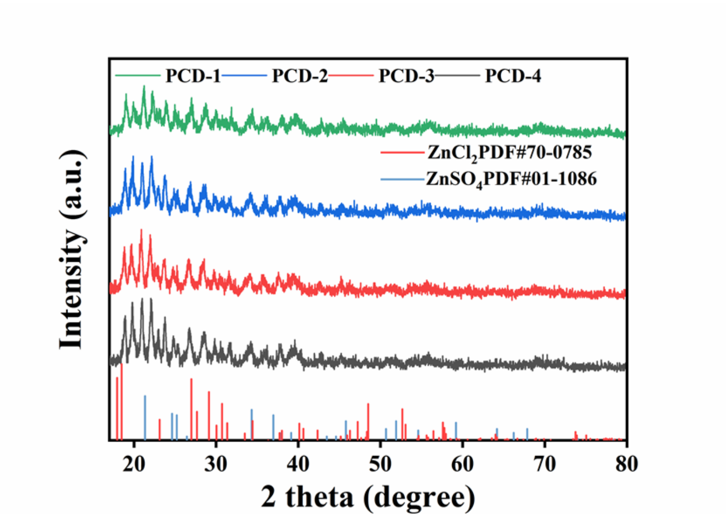


Figure S1. XRD patterns of PCD-1, PCD-2, PCD-3 and PCD-4.

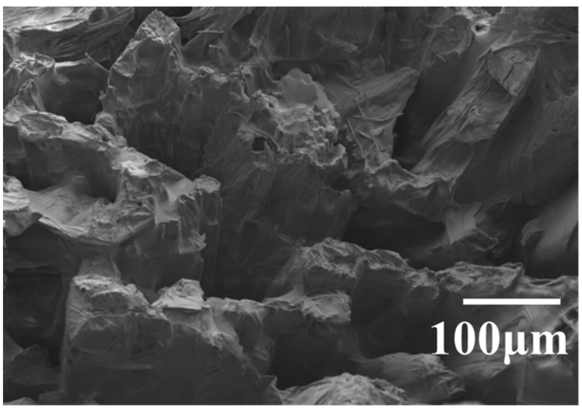


Figure S2. SEM images of PCD-4 at 100 μm resolution.

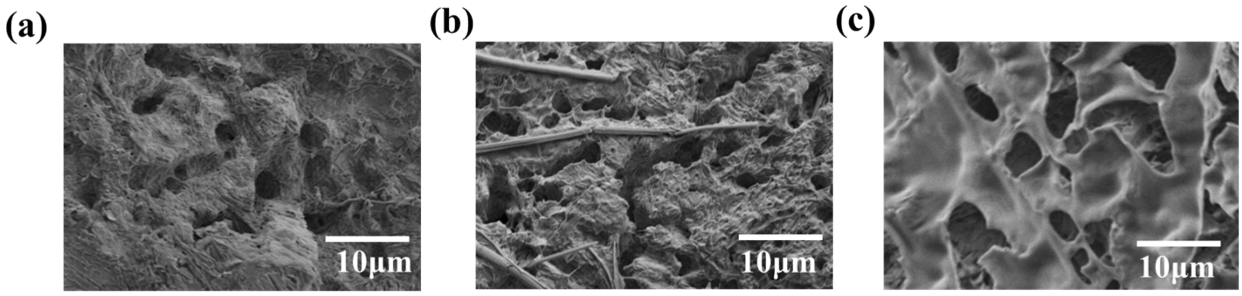


Figure S3. SEM images of (a) PCD-1, (b) PCD-2 and (c) PCD-3.

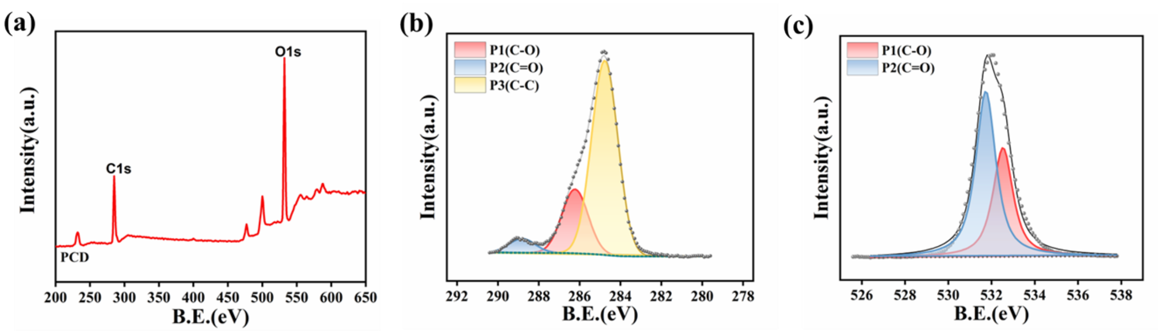


Figure S4 (a) XPS spectrum of PCD-4 sample. (b-c) XPS C 1s, O 1s of PCD-4 hydrogel.

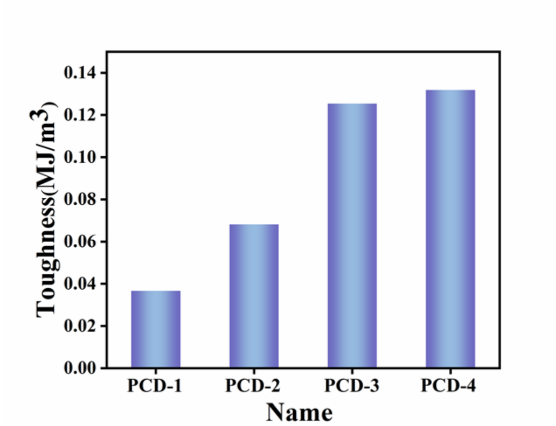


Figure S5 Toughness of hydrogels with different DMSO contents.

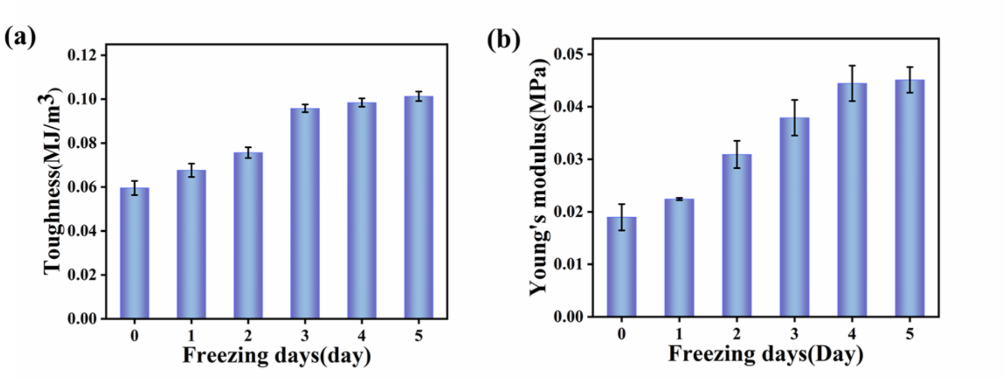


Figure S6 (a) Toughness, and (b) Young's modulus of PCD-4 hydrogel formed in different freezing days.

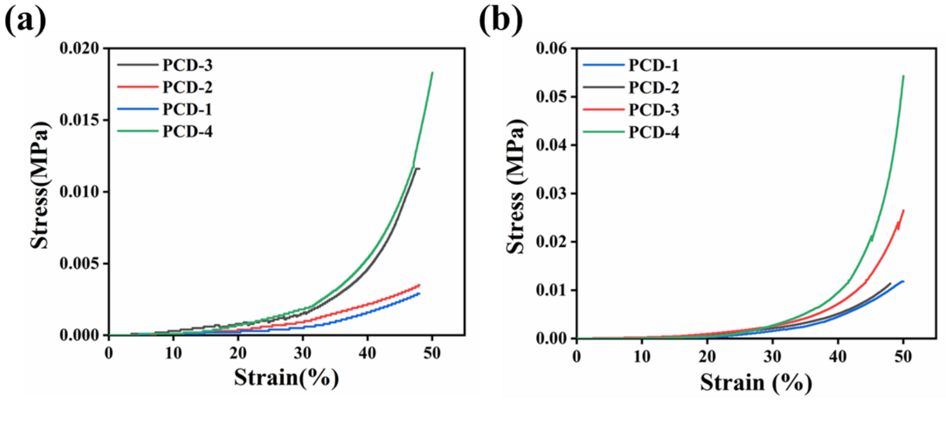


Figure S7 Stress-strain curves of hydrogels with different DMSO contents at a compressing rate of 3 mm min^{-1} at (a) room temperature and (b) -20 °C.

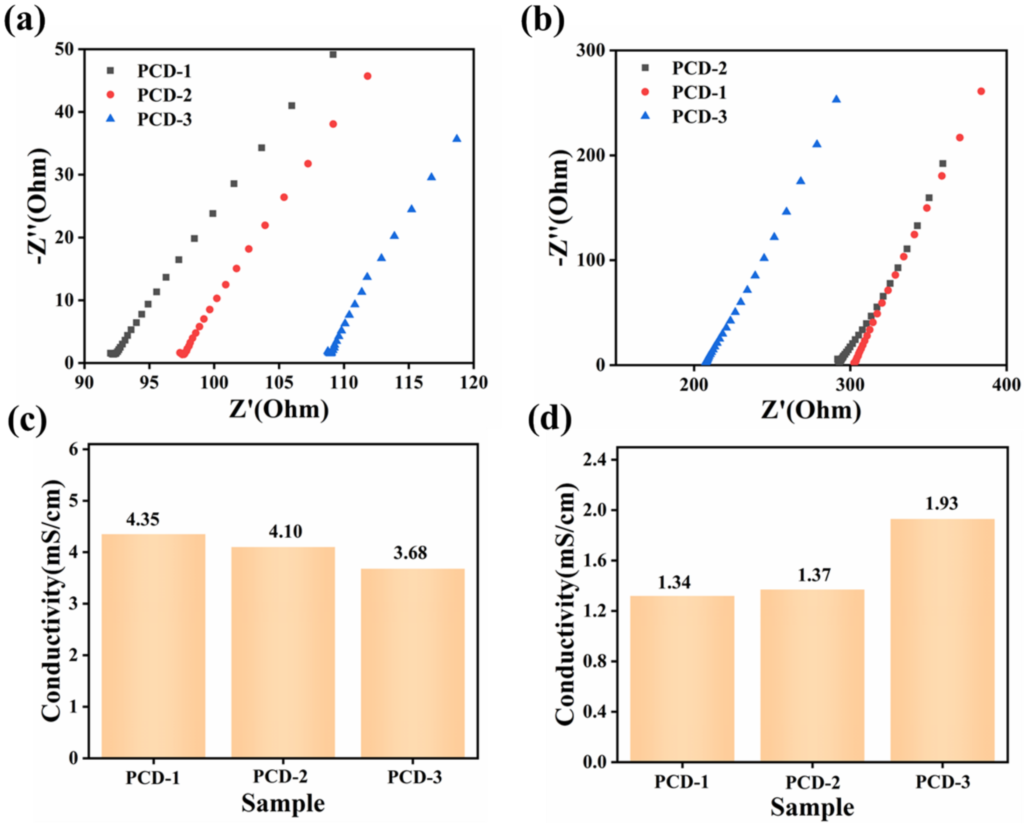


Figure S8 Nyquist plot of PCD hydrogels with different contents of DMSO at (a) room temperature (25 °C) and (b) -20 °C. Ionic conductivity of PCD hydrogels with different contents of DMSO at (c) room temperature (25 °C) and (d) -20 °C.

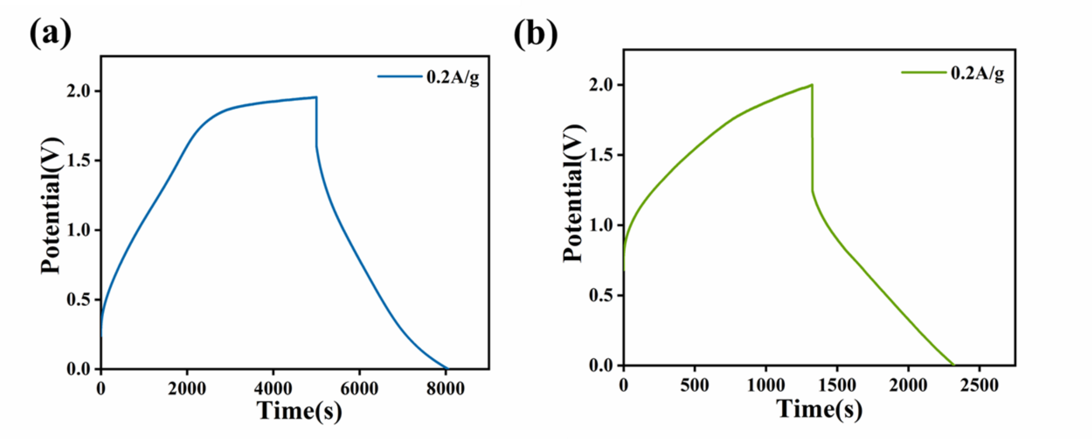


Figure S9 GCD curves at 0.2 A g^{-1} in (a) room temperature (25 ℃) and (b) -20 ℃.

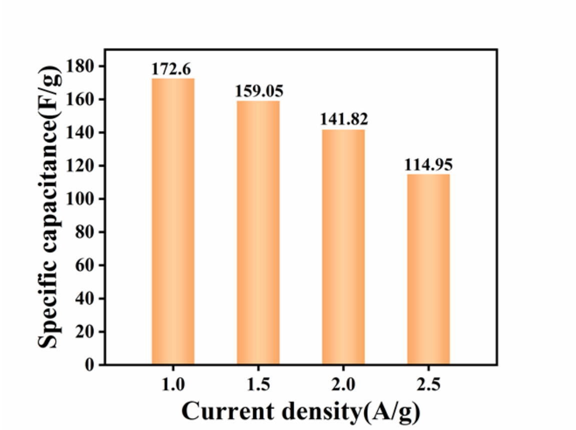
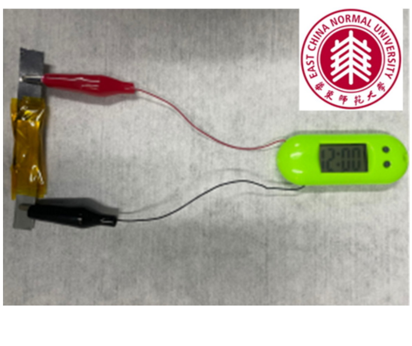


Figure S10 Specific capacity at current density of 1.0-2.5 A g^{-1}.



For 1 week

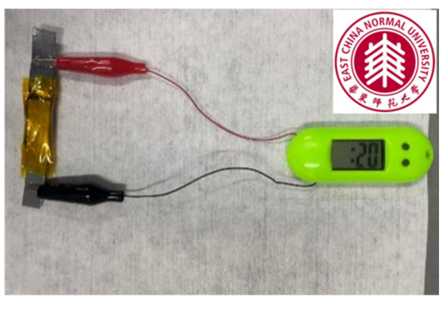


Figure S11 The best optimized FZHSC (a) can power an electric watch and (b) work for one week.

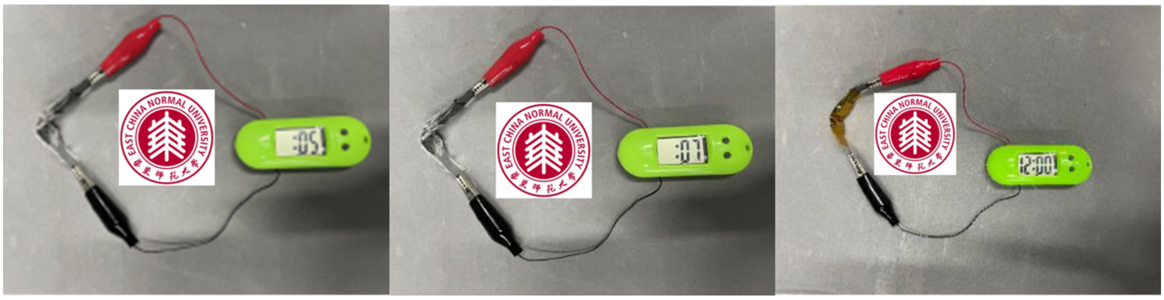


Figure S12 The bending device can power a watch.

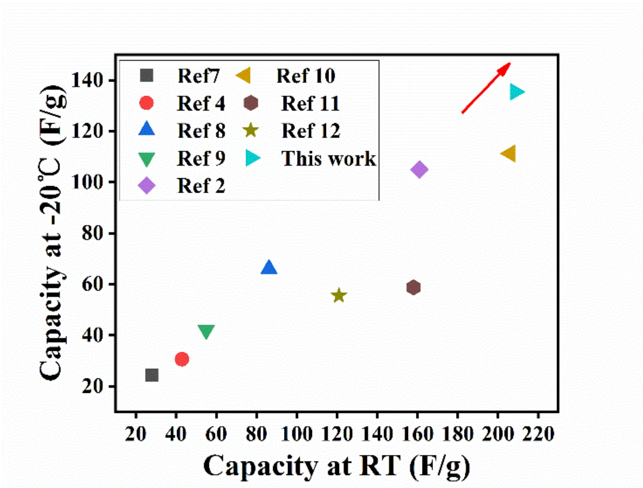


Figure S13 Capacity of the present supercapacitor and other anti-freezing supercapacitors reported in previous works.

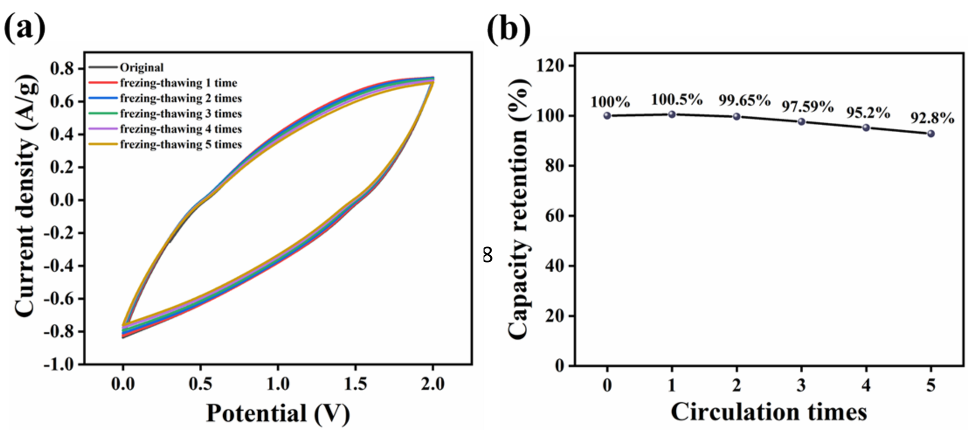


Figure S14 (a) CV curves and (b) capacity retentions of FZHSC after repeated freezing and thawing.

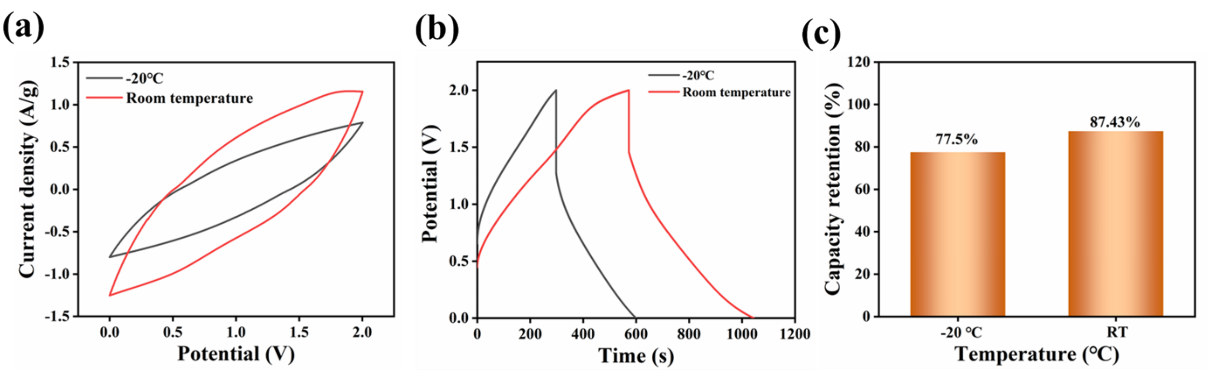


Figure S15 (a) CV, (b) GCD curves and (c) capacity retentions of FZHSC at different temperatures after freezing for a week.

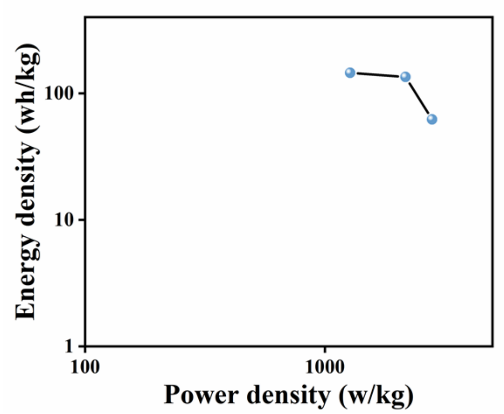


Figure S16 Ragone plot of FZHSC at -20 °C.

Table S1 The experimental ingredients and nomenclatures of the as-prepared hydrogels.

Name	H_2O(g)	PVA(g)	CNF(g)	DMSO(g)	$ZnSO_4$(g)
PCD-1	11	1.8	0.08	9	3.86(1.2M)
PCD-2	10	1.8	0.08	10	3.86(1.2M)

PCD-3	9	1.8	0.08	11	3.86(1.2M)
PCD-4	8	1.8	0.08	12	3.86(1.2M)

Table. S2 Comparison of the break elongation of PCD-4 hydrogel with previously reported hydrogel electrolytes.

Gel electrolyte	break elongation(%)	Ref
HPC/PVA/$LiClO_4$[a)]	247	[1]
MMT-PVA[b)]	13	[2]
PAMPS/PAAm/$ZnCl_2$/NH_4Cl[c)]	166	[3]
PAMPS/PAAm/LiCl[d)]	290	[4]
Lig/Gelatin[e)]	260	[5]
Starch/PVA/Glycerin/$CaCl_2$[f)]	254	[6]
PVA/CNF/$ZnSO_4$	362.7	This work

a) hydroxypropyl cellulose/poly(vinyl alcohol) (HPC/PVA) hydrogel with $LiClO_4$ water/glycerol mixture solution; b) montmorillonite/poly(vinyl alcohol) (MMT/PVA) hydrogel electrolyte. c) poly (2-acrylamido-2- methylpropane-sulfonic acid)/polyacrylamide (PAMPS/PAAm) double-network matrix and a binary solvent electrolyte system- ethylene glycol/H_2O (EG/H_2O with a water content of 10% v/v) containing $ZnCl_2$/NH_4Cl salts. d) PAMPS/PAAm double-network hydrogel soaked from 4 m LiCl/ethylene glycol. e) Lignin-based hydrogels were synthesized by using polyethylene glycol diglycidyl ether (PEGDE) as a macromolecular cross-linking agent through base-catalyzed ring-opening polymerization and cross-linking reaction between phenolic hydroxyl groups in lignin and epoxy group in PEGDE. f) starch/PVA/Glycerin/$CaCl_2$ (SPGC) organohydrogel.

Table S3 Comparison of the Capacity of PCD-4 FZHSC at room temperature (25 °C) and -20 °C.

ZHSC	Capacity at RT(F/g)	Capacity at -20 °C (F/g)	Ref
PVA/Agar-EMIMBF$_4$-Li$_2$SO$_4$-ZHSC	28	24.36	[7]
PAMPS/PAAm-ZHSC	43	30.53	[4]
PVA/ARS/ H$_2$SO$_4$-ZHSC	86.25	66	[8]
PAAK/CMC-x-ZHSC	55	42	[9]
MMT/PVA/H$_2$SO$_4$-ZHSC	161	105	[2]
PVA/MMT/Zn(ClO$_4$)$_2$-ZHSC	206	111.24	[10]
AF PVA-CMC/Zn(CF$_3$SO$_3$)$_2$	158	58.76	[11]
PAMPS/PAAm/ZnCl$_2$/NH$_4$Cl	121	55.5	[12]
PVA/CNF/ZnSO$_4$-ZHSC	208.51	135.4	This work

References

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