Supplementary information

Zinc ion trapping in a cellulose hydrogel as a solid electrolyte for a safe and flexible supercapacitor

Lvye Yang, Lian Song, Yi Feng, Mengjue Cao, Pengcheng Zhang, Xiong-Fei Zhang, Jianfeng Yao*

College of Chemical Engineering, Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Jiangsu Key Lab for the Chemistry & Utilization of Agricultural and Forest Biomass, Nanjing Forestry University, Nanjing, Jiangsu 210037, China. Email: jfyao@njfu.edu.cn

Experimental details

Preparation of cellulose hydrogel electrolyte: The cellulose hydrogel was synthesized based on previous studies [S1, S2]. Briefly, $ZnCl_2$ (9.87 g) and distilled water (3.63 g) were mixed together and heated in 65 ^oC to get a clear liquid. With keeping the same temperature, cotton linter pulp (0.2 g) and $CaCl_2$ (0.2 g) were added into the above liquid and stirred to completely dissolve to get a viscous liquid. Then, such viscous liquid was sonicated for removing the bubbles and 2 g of distilled water was further added for increasing the gelation speed to get the final hydrogel. The cellulose (cotton linter pulp) was got from Nantong Cellulose Fibers Company (Nantong, China), and it has a viscosity-average molecular weight of 11.9×10^4 g mol^{-1} and a α-cellulose content more than 96%.

Assembly of flexible zinc-ion hybrid supercapacitor: The flexible zinc-ion hybrid supercapacitor was assembled by sandwiching cellulose hydrogel electrolyte between two electrodes of zinc foil anode and activated carbon cathode. The cathode electrode was fabricated by mixing activated carbon, carbon black and polyvinylidene fluoride (dispersed in N-Methyl pyrrolidone with the mass content of 5 wt%) with a weight ratio of 8:1:1 and coating into a titanium foil (the mass of activated carbon loading on titanium foil is around 2 mg/cm^2). The activated carbon was produced by Nanjing XFNANO Materials Tech Co., Ltd. in China.

Assembly of zinc-ion hybrid supercapacitor with a nonwoven separator: The nonwoven cloth was first soaked in a 1.75 g/g $ZnCl_2/H_2O$ water-in-salt $ZnCl_2$ for half an hour. Then, the soaked nonwoven cloth was sandwiched by two electrodes of zinc foil anode and activated carbon cathode to fabricate the zinc ion hybrid supercapacitor.

Electrochemical measurements of assembled zinc-ion hybrid supercapacitors: Electrochemical working station (CHI 760e, Chenhua, Shanghai) was used to measure the electrochemical performance. Cyclic voltammetry (CV), Galvanostatic charge discharge (GCD) and Electrochemical impedance spectroscopy (EIS) techniques were conducted. EIS is tested from 100 kHz to 0.1 Hz with an amplitude of 5 mV. Energy density (E_g, W h kg^{-1}) and power density (P_g, W kg^{-1}) are calculated by $E_g=C_g\times(\Delta V)^2/(2\times3.6)$ and $P_t=E_g/\Delta t \times 3600$, respectively, where C_g (F g^{-1}) is the mass specific capacitance, ΔV is the electrochemical potential window. The capacitive performances were calculated according the mass of activated carbon loading on titanium foil. Before a normal test, the zinc-ion hybrid supercapacitor was first charged and discharged for 20 times at a current density of 1 A g^{-1} to get a stable state.

Ionic conductivity measurement of cellulose hydrogel: The EIS test for ionic conductivity was conducted by sandwiching the hydrogel between two stainless steel sheets. Ionic conductivity (σ, mS cm^{-1}) is estimated by an equation of $\sigma=1000L/(AR)$, where L (cm) is the hydrogel thickness, A (cm^2) is the effective area of hydrogel and R (Ω) is the intercept with the real axis of nyquist plot.

Characterizations: Scanning electron microscope of JSM-7600F (SEM, JEOL Ltd.) and X-ray diffraction (XRD, Rigaku MiniFlex II) were used to examine the morphology of the zinc anode electrode. Raman spectra (Thermo DXR532) were examined to determine electrolyte. A minimum of three specimens were used for tensile tests. The gel specimens (11 and 4 mm in width and thickness) were conducted by electromechanical universal testing machine (CMT850) with a stretching rate of 10 mm/min.

Table S1. The ambient ionic conductivity of different electrolytes used in electrochemical energy storage devices.

Electrolyte	State	Liquid salt solution and concentration [a]	Electrolyte matrix	Ionic conductivity
Cellulose hydrogel	Gel	$ZnCl_2$/1.75 g/g	Cellulose	74.9 mS cm^{-1}
HiSE [S3]	Gel	LiTFSI/10 M	Polyacrylamide and chitosan	51.3 mS cm^{-1}
Gelatin/$ZnSO_4$ gel [S4]	Gel	$ZnSO_4$/1 M	Gelatin	3.38 mS cm^{-1}
B-PVA/NFC hydrogel [S5]	Gel	$ZnSO_4$/2 M	Polyvinyl alcohol and nanocellulose	18.1 mS cm^{-1}
Ionogel [S6]	Gel	[DMIm][(MeO)(H)PO_3] and [BMIM][TFSI]	Cellulose	2.6 mS cm^{-1}
CMC gel [S7]	Gel	$LiPF_6$/1 M	Carboxymethyl cellulose	0.48 mS cm^{-1}
Zn_2SO_4	Aqueous	2 M	/	45.2 mS cm^{-1}
$ZnCl_2$	Aqueous	0.68 g/g	/	37.5 mS cm^{-1}
$ZnCl_2$	Aqueous	1.75 g/g	/	22.8 mS cm^{-1}
$ZnCl_2$	Aqueous	2.72 g/g	/	10.2 mS cm^{-1}

[a]: the concentration of $ZnCl_2$ is calculated based on the amounts of $ZnCl_2$ and H_2O.

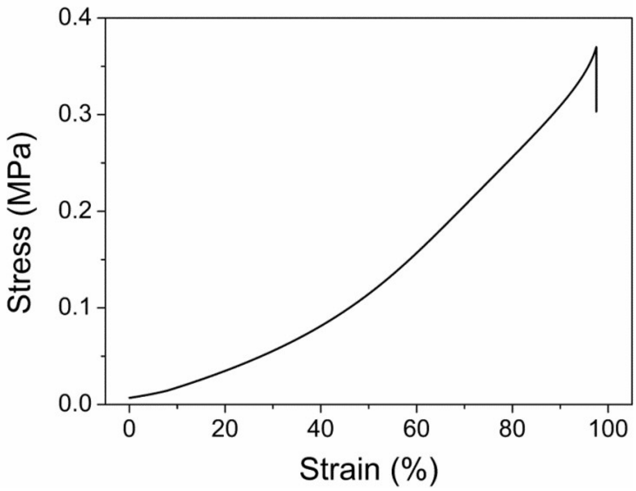

Fig. S1 Tensile stress–strain curve of the cellulose hydrogel.

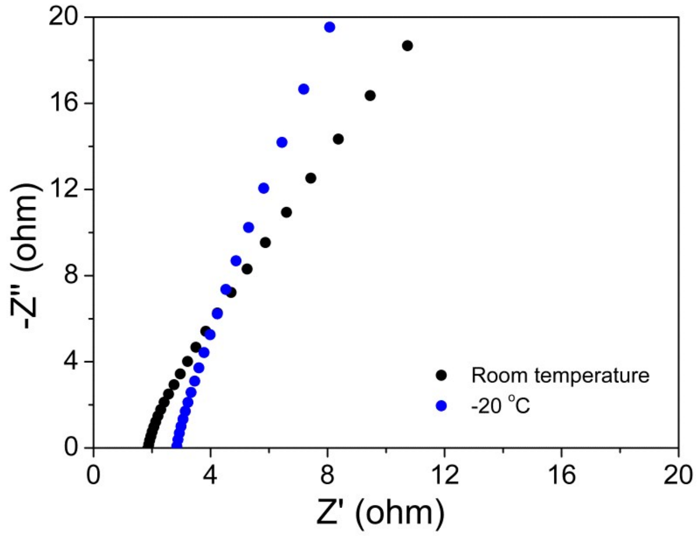

Fig. S2 The nyquist plot tested by sandwiching the cellulose hydrogel between two stainless steel sheets. The size of hydrogel is 0.2×1×1.5 cm^3 (thickness×width×length)

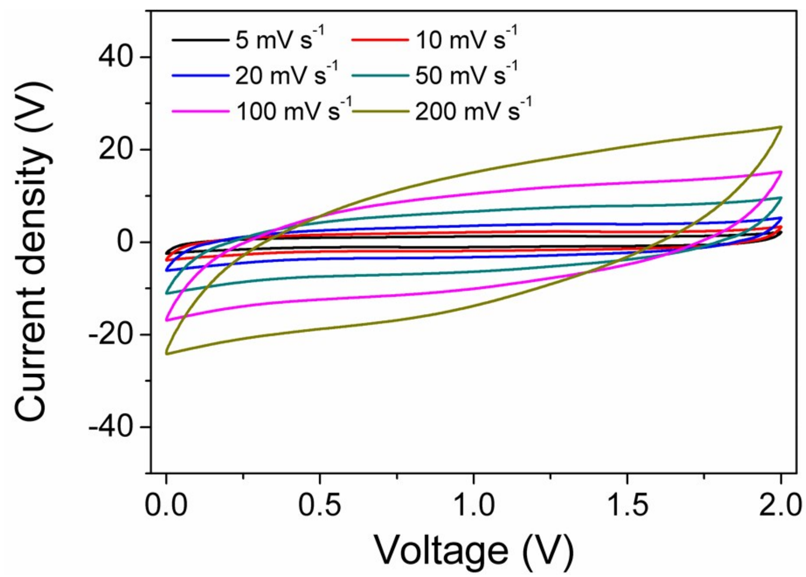

Fig. S3 The CV curves at different scan rates from 5 to 200 mV s^{-1} by testing the water-in-salt zinc-ion hybrid supercapacitor assembled with nonwoven cloth.

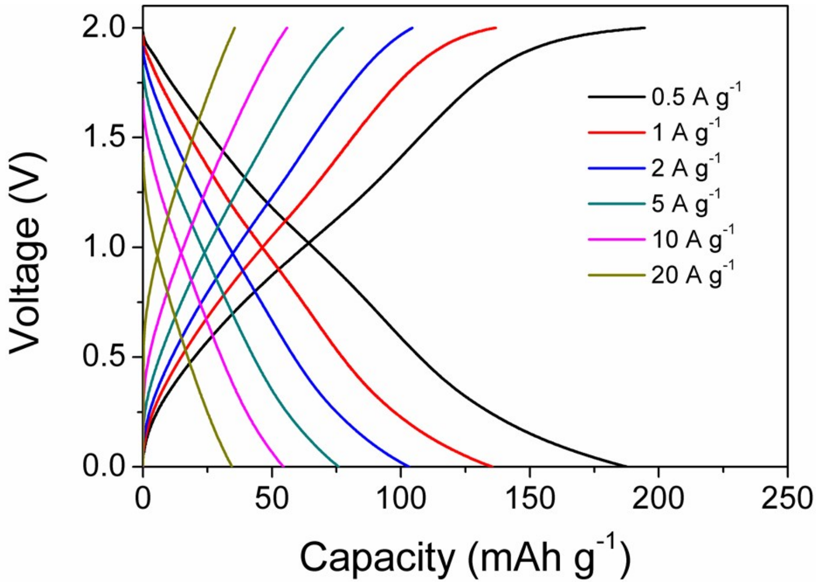

Fig. S4 The GCD curves at different current densities from 0.5 to 20 A g^{-1} by testing the water-in-salt zinc-ion hybrid supercapacitor assembled with nonwoven cloth.

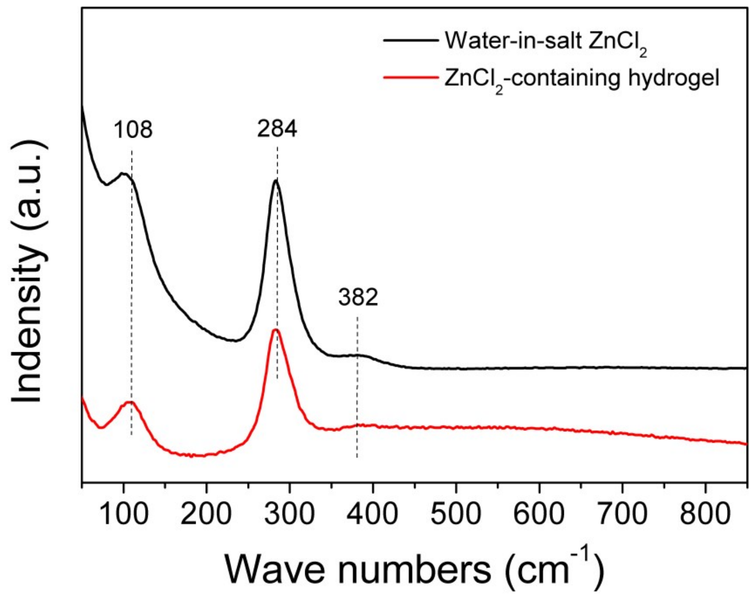

Fig. S5 Raman spectra of $ZnCl_2$ solution (1.75 g/g $ZnCl_2/H_2O$) and the cellulose hydrogel at the same $ZnCl_2$ concentration.

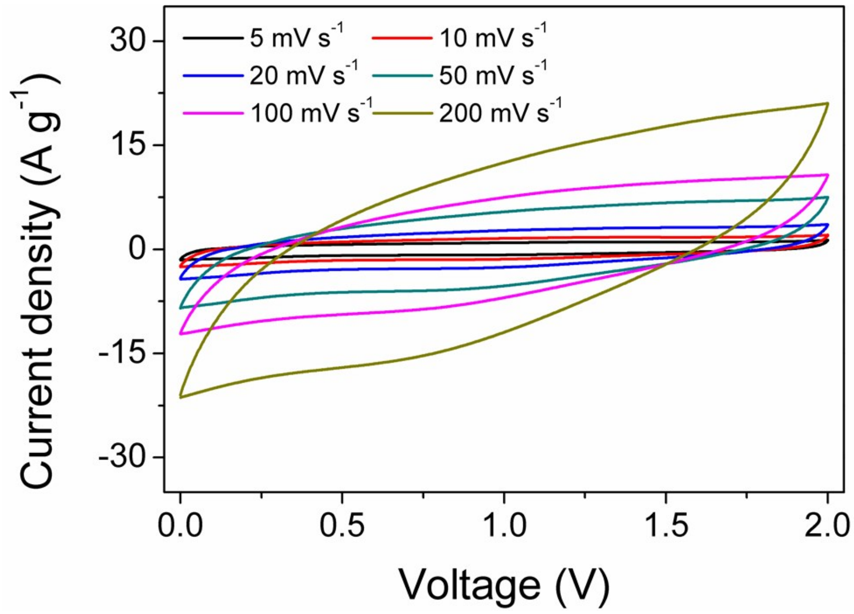

Fig. S6 The CV curves at different scan rates under a low temperature of -20 ^{o}C by testing zinc-ion hybrid supercapacitor assembled with cellulose hydrogel electrolyte.

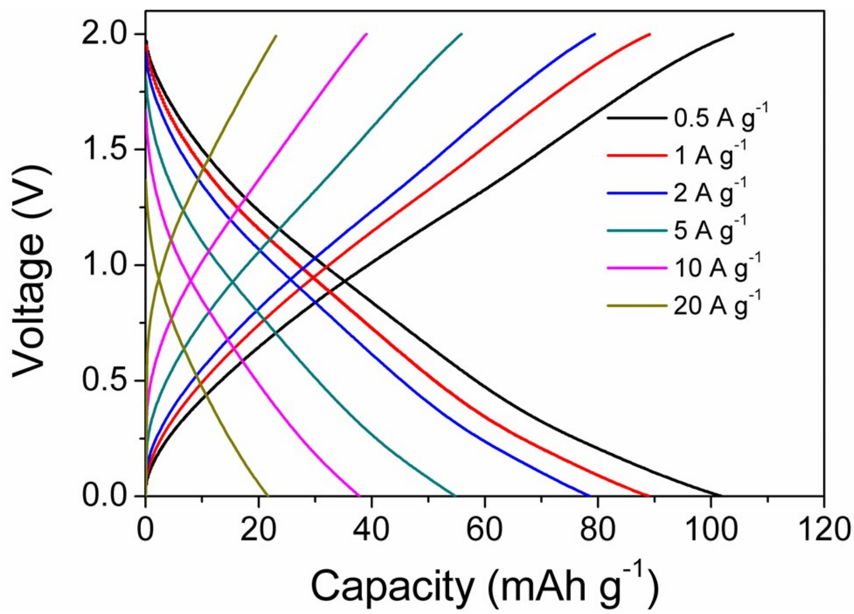

Fig. S7 The GCD curves at different current densities under a low temperature of -20 ^{o}C by testing zinc-ion hybrid supercapacitor assembled with cellulose hydrogel electrolyte. The coulombic efficiency is in the range of 94.0 - 99.8% at -20^{o}C.

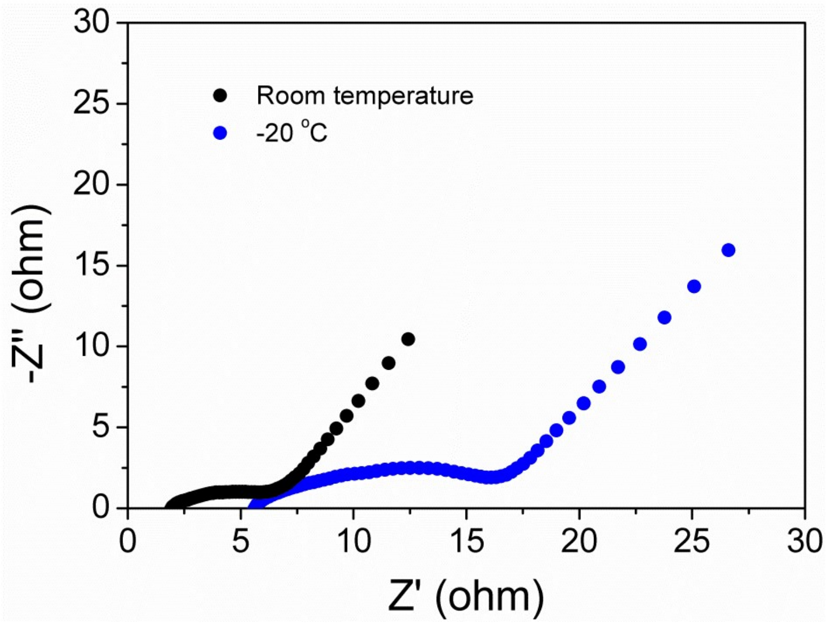

Fig. S8 The nyquist plots at the room temperature and -20 °C by testing zinc-ion hybrid supercapacitor assembled with cellulose hydrogel electrolyte.

Fig. S9 The flexibility of zinc-ion hybrid supercapacitor assembled by the cellulose hydrogel electrolyte.

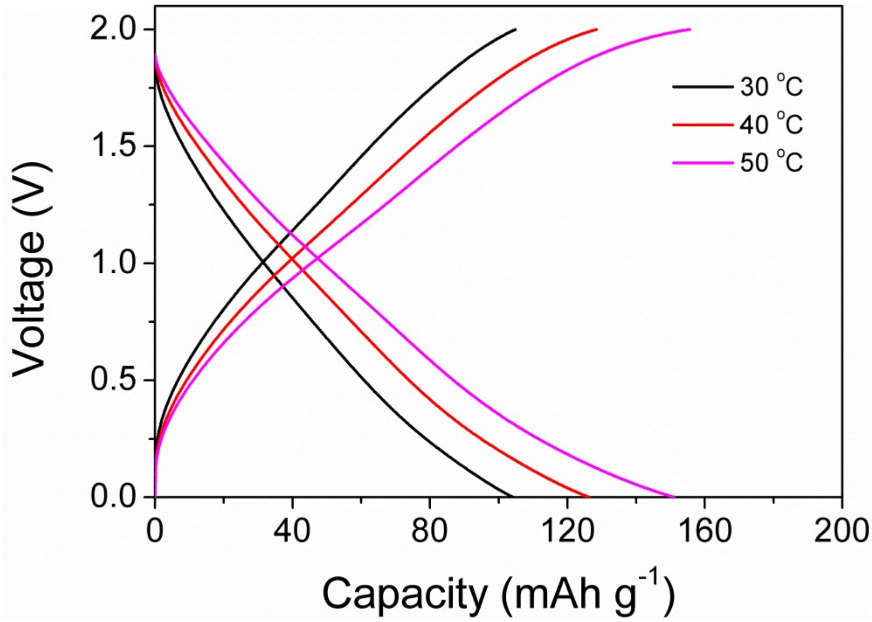

Fig. S10 GCD curves under the temperatures of 30, 40 and 50 °C at the current density of 5 A g^{-1}.

References

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