

Supplementary Information

Thermoresponsive gel polymer electrolytes for smart rechargeable zinc-ion batteries

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Reagents

N-isopropylacrylamide (NIPAM, 98%), 1-vinylimidazole (Vim, 99%), Acrylamide (AM, 98%) and zinc sulfate (ZnSO_4 , 98%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Poly (ethylene glycol) dimethacrylate (PEGDA, 98%), and 2-hydroxy-2-methylpropiophenone (1173, 98%) were obtained from Beijing J&K Scientific Ltd. All reagents were used without any purification. Deionized water was used throughout the experiments.

Fabrication of hydrogels.

Predetermined amounts of NIPAM, AM and Vim, were dissolved as monomers in deionized water, then cross-linker PEGDA (0.5 wt% to monomers) and photoinitiator 1173 (0.2 wt% to monomers) were added. The mixed precursors were transferred into quartz molds and exposed to UV light for 3 min at room temperature to obtain PNIPAM/AM/Vim hydrogels. A polymerized PNIPAM/AM hydrogel was prepared following the same method. The as-prepared PNIPAM/AM/Vim hydrogels were immersed in zinc sulphate aqueous solution (0.25 M) for 15 h to obtain PNIPAM/AM/Vim- Zn^{2+} hydrogels. Subsequently, the hydrogels were washed with deionized water to remove excess metal ions.

The water uptake (WU) and swelling degree (SD) of the hydrogels were calculated using the following equations:

$$WU (\%) = \frac{m_w - m_d}{m_w} \times 100$$

$$SD (\%) = \frac{X_w - X_d}{X_w} \times 100$$

where m_d and X_d were the weight and dimension of gels in dry state and m_w and X_w were the weight and dimension of gels in wet state.

Characterization of hydrogels.

Transmittance was measured by an Agilent Carry 5000 spectrometer from 400 to 800 nm with water as the reference. Temperatures were recorded by the Kaipusen thermocouple pyrometer. Fourier transform infrared spectrometer (FTIR) spectroscopy was performed using an FT/IR-6800 in the range of 400-4000 cm^{-1} . The surface wettability of gels was performed by OCA25 contact measuring system. Variable-temperature small-angle X-ray scattering (SAXS) characterizations of the hydrogel and deionized water (as background) were conducted on the SAXSess mc2 X-ray scattering system (Anton Paar) with $\text{Cu K}\alpha$ radiation (0.154 nm) operating at 40 mA and 50 kV. The pair distance distribution function (PDDF) was obtained by indirect Fourier transformation (IFT) of the SAXS profiles using the PCG program (3.01.10-58). The mechanical properties of evaluated using an AG-2000A tensile tester (Shimadzu) at room temperature. Standardized dumbbell-shaped samples ($1\times 10\times 20$ mm) were used for tensile testing with speed of 10 mm/min. The stress was calculated the load of per unit area and the strain was defined as the change in dimension relative to the original size of the specimen. Scanning electron microscopy (SEM) was carried out using a Hitachi Regulus Model 8100 instrument for imaging.

Electrochemical measurements.

Electrochemical impedance spectra (EIS) spectra were measured using a CHI760D electrochemical workstation (Shanghai Chenhua) by a two-electrode alternating current impedance method with a frequency range of 1 to 10^6 Hz and an oscillation voltage of 5 mV. All gel polymer electrolytes were assembled into CR2032 button cells with stainless steel as electrodes. Before measurements, the cells were put into an oven and allowed to stabilize for 1 h at different temperatures. The symmetrical cell with zinc electrodes and hydrogel electrolyte was also assembled into a CR2032 button cell. The Tafel curves and time-current plots were analyzed on a CHI760D electrochemical workstation (Shanghai Chenhua). Charge/discharge tests were conducted using a LANHE battery test system at different temperatures. The full cell was comprised of zinc flake as the anode, sodium vanadate ($\text{NaV}_3\text{O}_8\cdot 1.5\text{H}_2\text{O}$, NVO) as the cathode and hydrogel as the electrolyte. The cathode was prepared by coating a slurry containing

NVO, Super P, and polyvinylidene fluoride (PVDF) with a ratio of 7:2:1 on a carbon cloth using a film applicator.

The Zn^{2+} transference number was evaluated in symmetrical Zn battery combined with EIS before and after the chronoamperometry (CA) test and calculated by the following equation:

$$t_{Zn} = \frac{I_s(\Delta V - I_0 R_0)}{I_0(\Delta V - I_s R_s)}$$

where ΔV is the applied polarization voltage (25 mV), I_s and R_s are the polarized current and resistance, respectively, and I_0 and R_0 are the initial current and resistance, respectively.

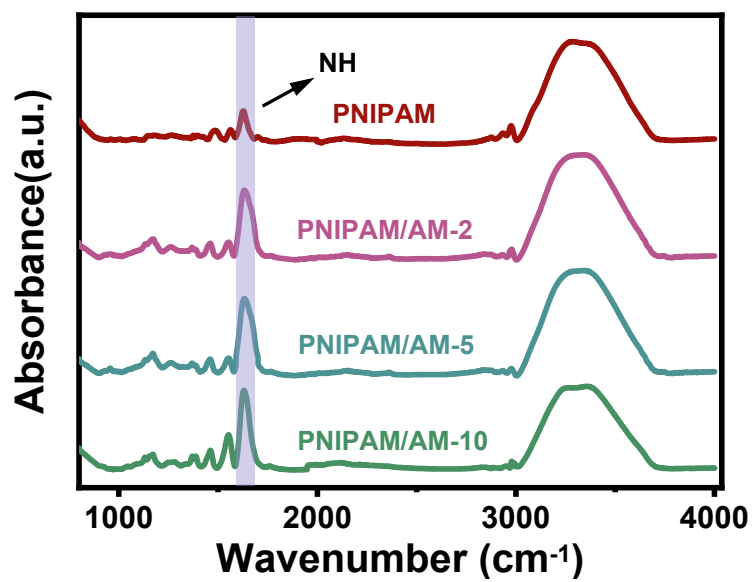


Fig. S1. FTIR spectra of PNIPAM/AM hydrogels with different AM content.

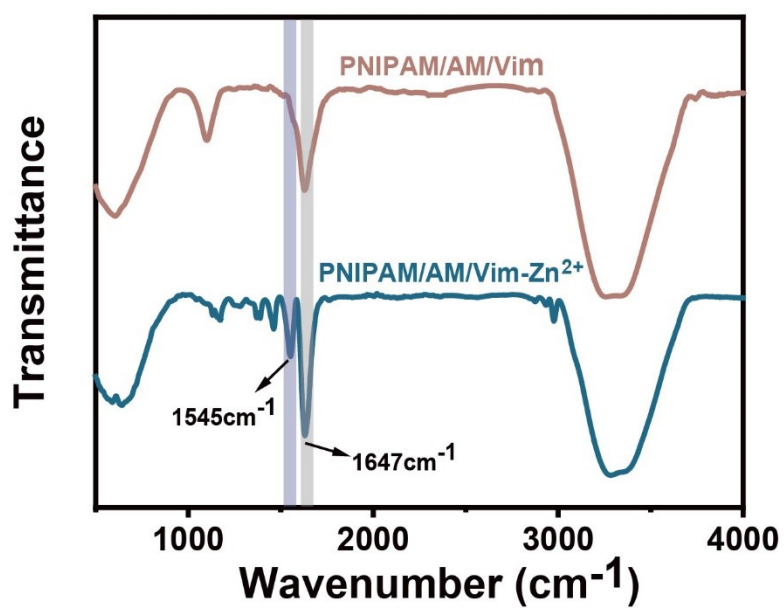


Fig. S2. FTIR spectra of PNIPAM/AM/Vim and PNIPAM/AM/Vim-Zn²⁺ hydrogels.

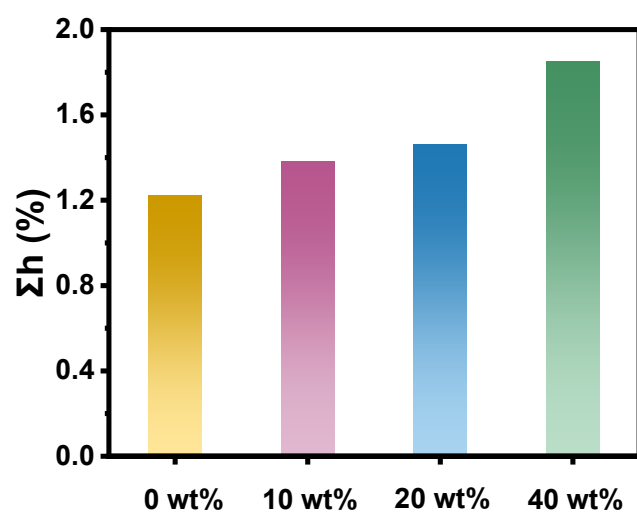


Fig. S3. The elongation at break of gel with different Vim content.

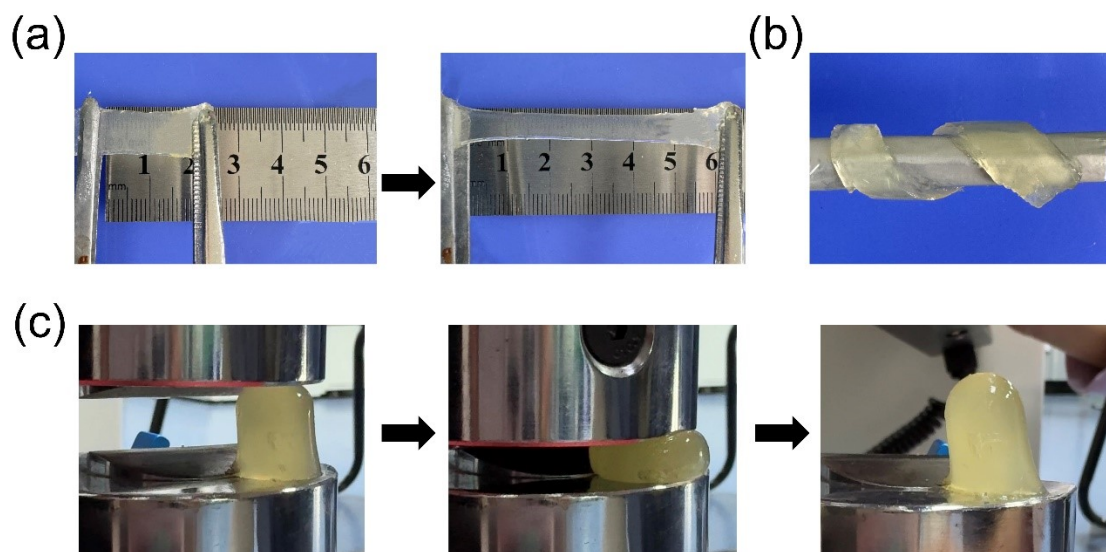


Fig. S4. Photographs showing that PNIPAM/AM/Vim- Zn^{2+} gels have high flexibility (a, b) and can withstand high level of compression (c).

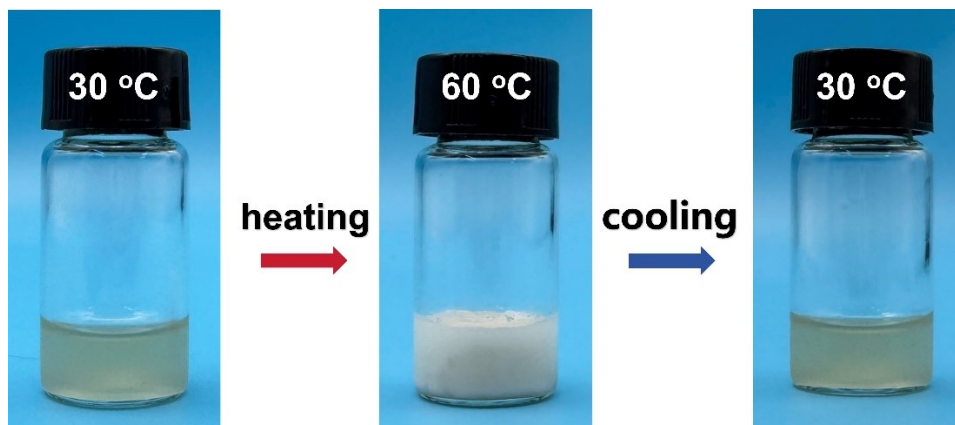


Fig. S5. Schematic diagram of the phase transition for PNIPAM/AM/Vim-Zn²⁺.

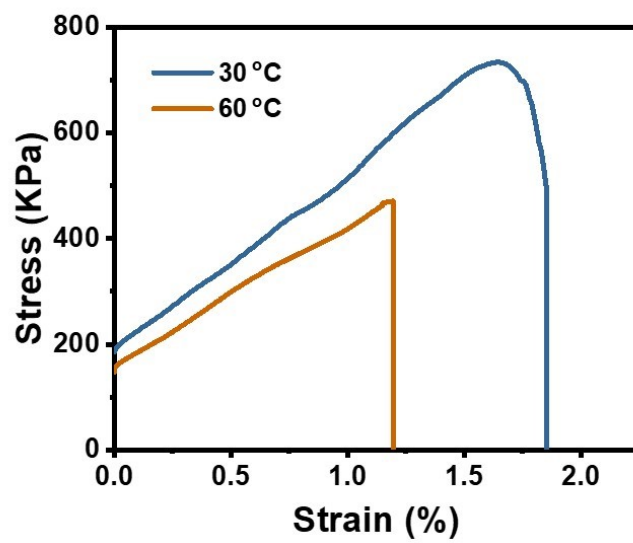


Fig. S6. Tensile stress–strain curves of PNIPAM/AM/Vim-Zn²⁺ hydrogel at different temperatures.

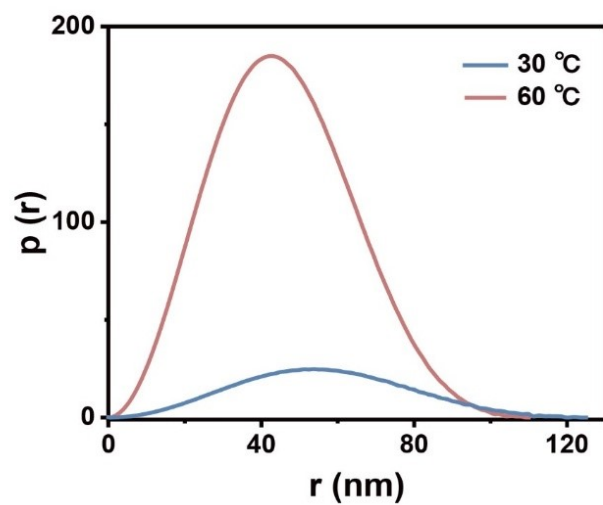


Fig. S7. PDDF of the PNIPAM/AM/Vim- Zn^{2+} hydrogel during the high-temperature phase transition.

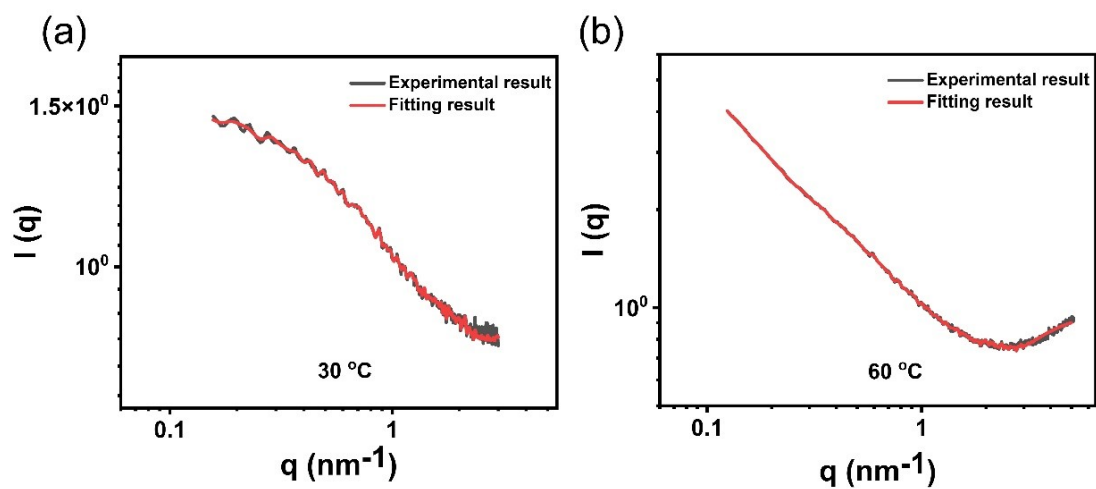


Fig. S8. Corresponding best approximation of SAXS spectrum at 30 °C and 60 °C.

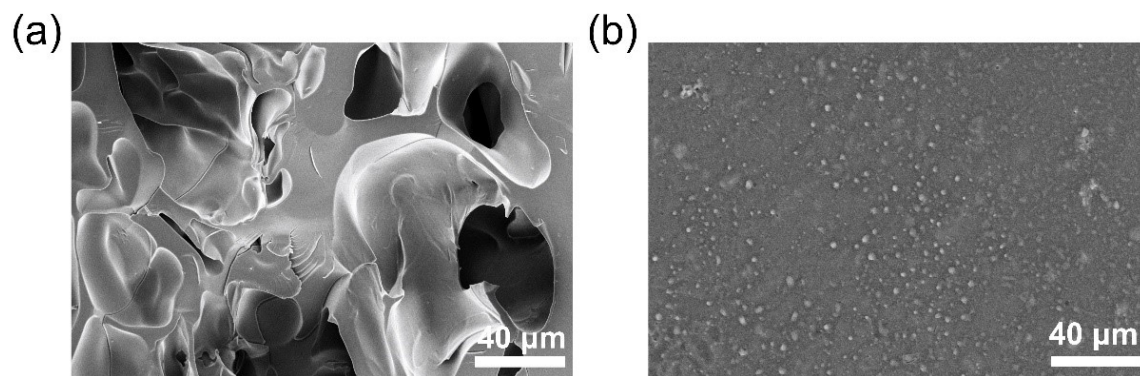


Fig. S9. The SEM images of PNIPAM/AM/Vim-Zn²⁺ gel electrolyte at (a) 30 °C and (b) 60 °C.

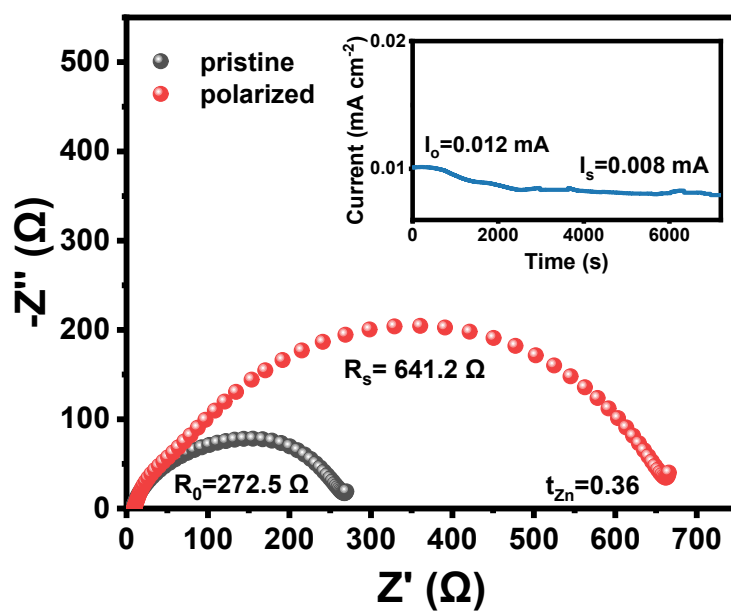


Fig. S10. Impedance spectra of Zn//Zn symmetric cells with PNIPAM/AM/Vim-Zn²⁺ gel electrolyte before and after voltage application, inset is time-current curve.

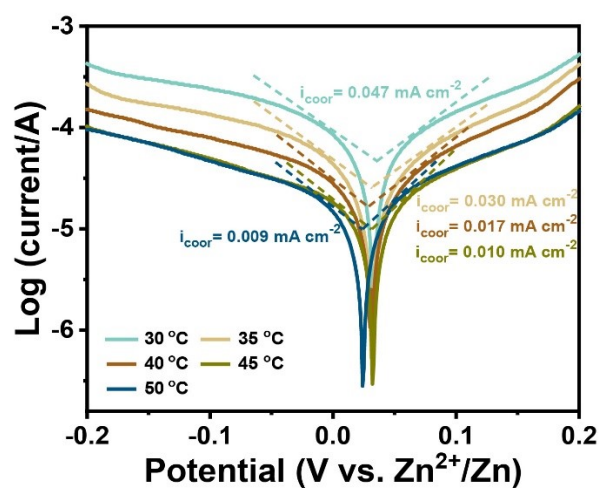


Fig. S11. The Tafel curves of PNIPAM/AM/Vim-Zn²⁺ gel electrolyte at different temperatures.

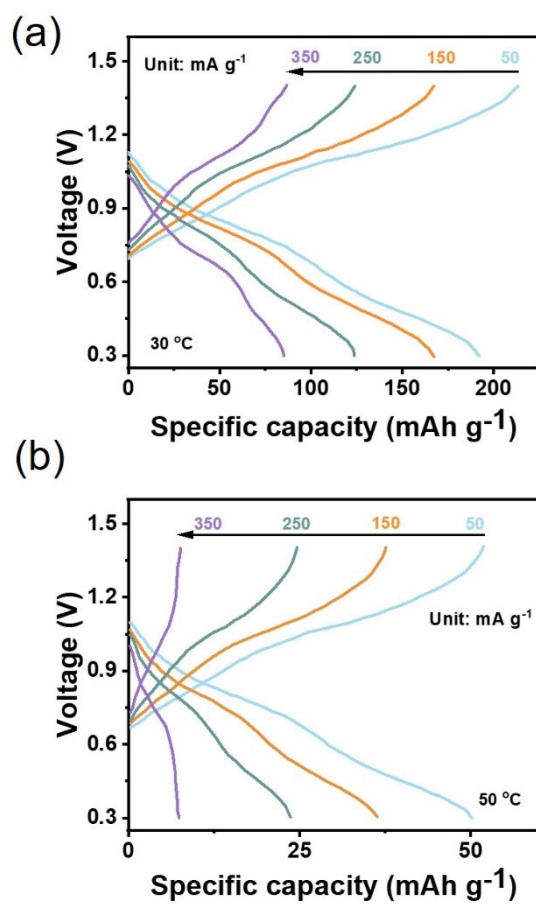


Fig. S12. Selected charge-discharge voltage profiles of Zn//NVO full cells at various current densities at (a) 30 °C and (b) 50 °C.

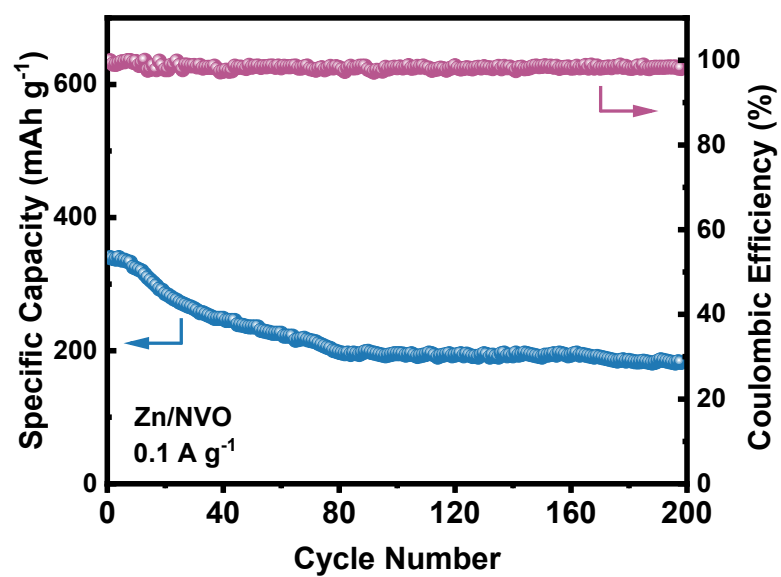


Fig. S13. Cycling performance of PNIPAM/AM/Vim-Zn²⁺ gel at 0.1 A g⁻¹.

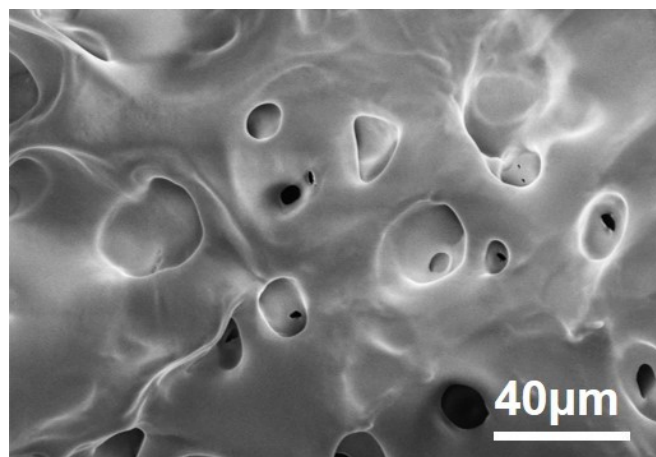


Fig. S14. SEM image of PNIPAM/AM/Vim-Zn²⁺ gel after cyclic testing.

Table S1. The water uptake of gel at different temperatures.

Temperature (°C)	Initial weight (g)	Final weight (g)	Average water uptake (%)
30	0.114	0.185	63
	0.133	0.214	
	0.121	0.199	
45	0.109	0.136	26
	0.114	0.144	
	0.124	0.157	
60	0.120	0.060	-50
	0.113	0.059	
	0.116	0.055	

Table S2. The swelling degree of gel at different temperatures.

Temperature (°C)	Initial volume (cm ³)	Final volume (cm ³)	Average swelling degree (%)
30	0.095	0.114	20
	0.113	0.136	
	0.102	0.122	
45	0.093	0.117	26
	0.112	0.141	
	0.111	0.140	
60	0.099	0.076	-23
	0.101	0.078	
	0.106	0.082	

Table S3. Comparison of reported thermoresponsive polymer electrolytes for protecting batteries from thermal runaway.

Polymer structure	Working mechanism	Trigger temperature	Ionic conductivity (S/cm)	Cycling performance
PEO-PPO-PEO [1]	Interruption of ion transport by gel-sol transition	Varied by tuning concentration or changing average molecular weight	7.80×10^{-4} (with 0.5M LiNO ₃) at room temperature	N/A
PEG [2]	Adsorption of heat by phase transition from crystalline to amorphous	Slow down the temperature rise speed	5.16×10^{-2} (with 1M ZnSO ₄) at room temperature	500 cycles for NVO//Zn full cell at room temperature
PAAm [3]	Reduction of ion diffusion rate by evaporation of water	50 °C	$\sim 4 \times 10^{-2}$ (with 1M ZnSO ₄) at 25 °C	500 cycles for MnO ₂ //Zn full cell at room temperature
PNIPAM [4]	Interruption of ion transport by gel-sol transition	Varied by tuning the concentration of hydrophilic part	N/A	500 cycles for MnO ₂ //Zn full cell at room temperature
PNIPAM (This work)	Interruption of ion transport by swelling-deswelling transition	Varied by tuning the concentration of hydrophilic part	4.81×10^{-4} (with 0.25M ZnSO ₄) at 30 °C	200 cycles for NVO//Zn full cell at room temperature

References

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