Supporting Information

Mechanoresponsive elastomeric binder toughened by supramolecular zwitterionic network for silicon anodes

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Experimental section

Materials: Acrylic acid (AA, >99 %, Aladdin), [2-(Methacryloyloxy)ethyl]dimethyl-(3-sulfopropyl)ammonium hydroxide (SBMA, 99%, HEOWNS, M_w~279.35), Carboxymethyl Cellulose (>99%, Aladdin), ammonium persulfate (APS, >98%, Aladdin), polyacrylic acid (PAA, Aladdin, M_w~450,000), silicon powder (99.9%, MERYER, average particle size of 1 μ m), carbon nanotubes (CNTs, 95%, Aladdin), electrolyte for Li-ion batteries (1 M LiPF₆ in EC/DEC = 1:1 vol% with 5.0% FEC, Suzhou DoDoChem). All chemicals were used as received without further purification.

Synthesis of PAA-SBMA: The 0.2 g SBMA was added to deionized water and then ultrasonically dispersed in 5 mL of ultra-pure water with a probe for 20 minutes. The above suspension was added to 0.8 g AA solution containing 2.0 g APS (5 wt%) and stirred at 80 to obtain a transparent, uniform and viscous solution. PAA-SBMA composite was obtained by drying the suspension in vacuum oven at 80°C after several days of dialysis in ultra-pure water. In contrast, the preparation method of PAA composites is the same as that of PAA-SBMA, except that SBMA is not added.

Preparation of electrodes: In the process of preparing Si electrodes, Si microparticles, carbon nanotubes (CNTs) and polymer binder are mixed in ultrapure water according to the mass ratio of 80:10:10 to obtain a uniformly dispersed slurry. PAA and PAA-SBMA were selected as binders respectively. The slurry is coated on the surface of the collector and dried in a vacuum drying oven at 80°C for more than 12 hours. The electrodes are cut into discs with a diameter of 12 mm. The normal-loading and high-loading of the active materials (SiMPs) were ~1.1 and 2.4 mg cm⁻², respectively.

Cells assembly: The CR2025 battery is assembled in a dry glove box filled with argon with less than 0.1 ppm of water and oxygen. 1M LiPF₆ was used as electrolyte in ethylene carbonate (EC) and carbonate (DEC) (1:1 by volume) and fluotene carbonate (FEC, 5% by volume), and Celgard 2500 membrane as separator. A half battery is assembled with a lithium sheet as a counter electrode. The coin-type full battery was assembled with Si@PAA and Si@PAA-SBMA as the anodes. Each coin type battery uses 80 µL electrolytes. The n/p ratio based on the capacity ratio between the anode and cathode was about 1.2.

Electrochemical measurements: To evaluate electrochemical performance of

coin-type cells, galvanostatic charge-discharge tests of the half cells were carried out using LAND Test System between 0.01 and 1.5 V. Cyclic voltammetry was recorded by an electrochemical workstation (Gammary) in the voltage range of 0.01–1.5 V (vs. Li/Li⁺) with different scan rates. The Li-ion diffusion coefficient of Si electrodes with various binders is evaluated by the slopes obtained by the cathodic-anodic peak currents and square root of scanning rates linear fitting, which was demonstrated by the Randles-Savcik equation if the solution is at 25°C. $I_p = (2.69 \times 10^5) n^{1.5} A C_{IJ} + D_{IJ} + 0.5 v^{0.5}$

where ${}^{I_{p}}$ is the peak current, n is the number of electron transfer, A is the working electrode area, ${}^{C}{}_{Li}{}^{+}$ is the Li-ion concentration in the electrolyte, ${}^{D}{}_{Li}{}^{+}$ is Li-ion diffusion coefficient, v is the scanning rate. When n, A and ${}^{C}{}_{Li}{}^{+}$ are known as a constant value during cycling in general, the slope of the linear relationship between ${}^{I_{p}}$ and ${}^{v_{0.5}}$ has a positive correlation with ${}^{D}{}_{Li}{}^{+}$. Galvanostatic intermittent titration techniques (GITT) of the half cells were performed on LAND Test System between 0.01 and 1.5 V. During the charging/discharging processes, a constant current of 0.2 C was applied for 10 min, and then 30 min rest intervals. The Li-ion diffusion coefficient can also be calculated using the following equation in accordance with Fick's second law:

$$D_{Li^{+}} = \frac{4}{\pi t} \left(\frac{m_B V_m}{M_B A} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

where *t* is the charging (discharging) time. m_B , V_m and M_B stand for the mass, molar volume and molar mass of the electrode, respectively. *A* is the effective surface area of contact between electrode and electrolyte. ΔE_s is the voltage change during the pulse. ΔE_t is the voltage change during the constant current charge (discharge). Electrochemical impedance spectroscopy (EIS) was performed on the same electrochemical workstation in the frequency range of 0.01–100 kHz. The full-cell measurements were activated in the initial first cycles on LAND Test System at 0.1 C, and then were charged in the voltage range of 2.0 and 4.5 V at 0.2 C.

Characterization: FTIR spectra were recorded on a Bruker Tensor II Fourier transform infrared spectrometer that equipped with a Specac Golden Gate ATR heating/cooling cell in the range of 4000-600 cm⁻¹. The temperature-dependent FTIR data were performed to proceed 2D correlation analysis. The software 2D Shige was used to analyse raw data in the scheduled wavelength ranges. DSC measurements were carried out on a TA DSC-25 instrument at the heating rate of 10 °C min⁻¹ in the range between 0°C and 160°C. The rheology measurement was performed by the rotary rheometer (HAAKE, MARS 60) at 25°C to identify the viscosities of different binder solutions at different shear rates. Strain-stress experiments were carried out using a Shimadzu AGS-X tester, which of a strain rate was controlled as 100 mm min⁻¹. The size of polymer specimens was 20 mm length × 5 mm width × 0.2 mm thickness at ambient conditions. Peeling tests were conducted on the Shimadzu AGS-X tester. The specimens were attached to 3M tapes based on a copper plate. The copper plate was fixed on the below clamp of tester and one end of 3M tape was fixed on the upper clamp at a constant displacement rate of 60 mm min⁻¹. Contact angles were performed by a KINO contact angle tester. The surface images of the Si electrodes before and after cycling were observed on AFM (Bruker Multimode 8). The surface morphologies and cross-section SEM images were performed by using a JEOL 7800F field emission electron microscope. Peak Force QNM AFM (Dimension Icon, Bruker) experiments were performed to measure mechanical property of the electrodes. The adhesion, Young's modulus, and energy dissipation of various electrodes were calculated from the gained force curves using the DMT model.

Molecular dynamics (MD) simulation: A periodic model of PAA-sulfobetaine elastomer containing one PAA chain (20 repeating units) and 20 sulfobetaine molecules was constructed in the Amorphous Cell module of Materials Studio, ver. 2019. The structure optimization and the calculation of potential energies were performed in the Forcite module. Cell parameter adjustment and re-optimization were employed to simulate the stretching process.

Density Functional Theory (DFT) Calculation details and simulations: To simulate interfacial configuration between polymer matrix and Silicon electrode, we implemented molecular dynamic simulations of material systems by Material Studio 2018 software. To simplify the model, one repeated unit of PAA molecule was constructed. The structures of PAA, PAA-SBMA and Silicon electrode were built and geometrically optimized using the Forcite module. The whole systems

were modeled with a minimum initial energy and a universal force flied at 300 K. According to final conformation model, the binding energy was calculated by the following equation:

 $E_{bind} = E_{poly} + E_{Si} - E_{total}$

in which E_{bind} is the binding energy between polymer matrix and Silicon electrode

layer, E_{poly} and E_{Si} represent the corresponding energy of polymer and Si, E_{total} stands for the total energy of PAA and PAA-SBMA composites.

To simulate the interactions between the binder and active materials, we carried out density functional theory (DFT) calculations using Vienna ab initio simulation package. When the vacuum layer was set to 15 Å, we built a 3×3 Si unit cell and geometry optimized for the structure of the fragments. The absorption energy was computed by the following formula:

 $E_{abs} = E_{substrate \, + \, molecule} - E_{substrate} - E_{molecule}$

where E_{abs} is the absorption energy between different functional group and Si particles. $E_{substrate + molecule}$ is the total energy of the whole system, $E_{substrate}$ and $E_{molecule}$ are the corresponding energy of Si substrate and the isolated molecules.



Figure S1. Preparation process of PAA-SBMA binder.



Figure S2. ATR-FTIR spectra of PAA, SBMA, and PAA-SBMA.



Figure S3. PAA-SBMA elastomer can be dissolved in water in 18 h.



Figure S4. The toughness and Young's modulus of samples with different contents of SBMA.



Figure S5. Stress-strain curves of the Si@PAA-SBMA electrodes with different contents of SBMA.



Figure S6. Optical images of PAA-SBMA films before and after stretching.



Figure S7. The contact angles of electrolyte on (a) PAA, (b) PAA-SBMA binders.



Figure S8. (a) Photographs of the PAA-SBMA self-healing process under dry conditions. (b) Self-healing photographs of PAA-SBMA under trace electrolyte (LiPF₆, 1mg cm⁻²) conditions. (c-e) Stress-strain curves of PAA-SBMA samples before and after self-healing in dry conditions (23% humidity) (c), trace electrolyte conditions (d), and humid environments (80% humidity) (e).

The calculation equation for healing efficiency is as follows:

$$\eta_{heal} = \frac{T}{T_0} \times 100\%$$

where η_{heal} is healing efficiency, T is the toughness after healing and T0 is the original toughness.



Figure S9. (a-b) Self-healing process of the PAA-SBMA elastomer was observed by the optical microscope, and the artificial scratches on the PAA-SBMA film were placed for 6 h at RH 20% (a) and trace electrolyte conditions (LiPF₆, 1mg cm⁻²) (b).



Figure S10. The average peeling forces of various electrodes.



Figure S11. Peeling test and photographs of different electrodes after peeling.



Figure S12. Digital photographs of (a) Si@PAA-SBMA, (b) Si@PAA electrodes after being folded different times, and unfolded states.



Figure S13. Digital photographs of (a) Si@PAA-SBMA, (b) Si@PAA electrodes immersed in water after being folded different times, and unfolded states.



Figure S14. Diagram of the nano-indentation experiment.



Figure S15. The galvanostatic discharge/charge voltage profiles of (a) Si@PAA-

SBMA, (b) Si@CMC and (c) Si@PAA electrodes at various current densities.



Figure S16. The galvanostatic discharge/charge voltage profiles of (a) Si@PAA-SBMA, (b) Si@CMC and (c) Si@PAA electrodes after different cycles at 2 A g⁻¹.



Figure S17. Cyclic performance of different electrodes at a current density of 1.0 A g^{-1} .



Figure S18. (a) The cycling performance of Si@PAA-SBMA electrodes with different SBMA contents at 2.0 A g⁻¹. (b) The initial galvanostatic discharge/charge profiles of these electrodes with different contents. The galvanostatic discharge/charge voltage profiles of Si@PAA-SBMA electrodes with contents (c) 1.0 wt%, (d) 5.0 wt%, (e)10 wt%, (f) 15 wt% and (g) 20 wt% SBMA after 3, 50 and 100 cycles.



Figure S19. The galvanostatic charge-discharge profiles of Si@PAA-SBMA||NCM811 full cell at 0.05 C and 0.2 C.



Figure S20. The rate performance of Si@PAA-SBMA full cell at 0.1 C, 0.2 C, 0.5 C, 0.7 C and 1.0 C.



Figure S21. The EIS curves of Si@PAA electrode after activation, 1, 50, and 100 cycles.



Figure S22. The CV curves of Si@PAA anode at different scanning rates from 0.2 to 1.0 mV s⁻¹.

 Table S1. Performance comparison between PAA-SBMA and other reported binders.

Binder	Mass loading (mg cm ⁻²)	Cycle number	Rate (A g ⁻¹)	Capacity (mAh g ⁻¹)	Ref.
PR-CNF	~1	150	2	998	3
		300	4	874	
PCSi	1.1	500	1	1129	21
P13	~1.3	300	2	734	28
PR-PAA	1.05	400	1.25	1611	38
SHP	0.6	100	1	2639	52
PU-PDA	0.3-0.5	300	2	959	53
OG@RGO	1.3	150	2	1750	54
MSi/CMC/TU120–2	0.8-1.0	150	0.8	1059	55
PAA-SBMA	~1.1	400	2	1625.1	This work
		300	4	1493.8	
		200	1	2234.2	