Supporting Information for

Water-soluble binder in high-performance silicon-based anode for lithium-ion batteries based on sodium carboxymethyl cellulose and waterborne polyurethane Xingshen Sun,^{+a,b,c} Xiangyu Lin,^{+b,c} Yong Wen,^b Fuhao Dong,^c Lizhen Guo,^c Zhanqian Song,^c Zitao Yang,^a He Liu,^c Xuequan Li,^{*a} Xu Xu^{*b} and Hongxiao Wang^{*c}

^a Key Laboratory of Green Chemical Technology of Fujian Province University; Fujian Provincial Key Laboratory of Eco-Industrial Green Technology; Department of College of Ecology and Resource Engineering, Wuyi University, Wuyishan 354300, China

^b Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

^c Institute of Chemical Industry of Forest Products, CAF; Key Lab. of Biomass Energy and Material, Jiangsu Province; Key Lab. of Chemical Engineering of Forest Products, National Forestry and Grassland Administration; National Engineering Research Center of Low-Carbon Processing and Utilization of Forest Biomass; Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing 210042, China

* Corresponding authors:

Xuequan Li, email: lixuequan@wuyiu.edu.en, phone: 086-0599-5136976 Xu Xu, email: xuxu200121@hotmail.com, phone: 086-25-85428369. Hongxiao Wang, email: wanghongxiao_1@163.com, phone: 086-25-85482452.

‡ These authors contributed equally to this work.

1.1. Electrolyte Uptake

The evaluation method for the swelling ratio of the binders was as follows: the masses of dry binders were measured (M_0), and each binder was then immersed in a binary solvent of ethylene carbonate (EC) and diethyl carbonate (DEC) (v/v, 3/7) with 5 vol% fluoroethylene carbonate (FEC) as an additive. After 40 hours, the electrolyte on the surface of the binder was quickly wiped out, and its mass was then measured (M_1). The swelling ratio was then calculated using the following equation:

Swelling ratio(%) =
$$\frac{M_1 - M_0}{M_0} \times 100 (\%)$$
 (I)

1.2. Contact angle

A double-sided adhesive (1.2 cm in width and 5 cm in length) was stuck to a steel plate (4 cm in width and 10 cm in length), and then the conductive carbon black was spread onto the double-sided tape to measure the contact angle between solution and the conductive carbon black. All the binders were dissolved in deionized water with a mass fraction of 0.5%.

1.3. Galvanostatic intermittent titration (GITT)

The GITT test was applied to estimate the diffusion coefficient of Li⁺ in the electrode material as follows: battery was first pre-cycled for 3 cycles at 0.05C (1 C = $3800 \text{ mAh } \text{g}^{-1}$), then a small current (0.03C) was used and kept constant for some time (20 min) and then cut off for 120 min. The change of electrode potential with time after the current cut-off was recorded.

According to the GITT results and Fick's second law, the following relation can

calculate the Li⁺ diffusion coefficient.

$$D_{Li}^{} + = \frac{4}{\pi\tau} \left(\frac{n_B V_m}{S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2 \tag{II}$$

where the S and τ stand for the surface area and relaxation time, respectively. V_m and n_B represent the molar volume and amount of substance of the electrode material, respectively. ΔE_{τ} represents the voltage change and ΔE_s is the pulse-induced voltage change.

1.4. SEM and XPS analyses of the electrode

The SEM and XPS analyses of the electrode were investigated as follows: after running the cycle performance of the Si electrodes for 50 cycles at 0.5C, the coin-cell was dissembled inside of the glove box, and the electrodes were washed with a binary solvent of EC and DEC three times. Then, each electrode was immersed in 20 mL of DEC for 48 h to remove the electrolyte from the electrode. Finally, the dry electrodes were analyzed using the SEM and XPS.



Fig. S1. Characterizations of Si/C particles. (a) SEM image. (b) Particle size distribution. (c) XPS spectrum. (d) Raman spectrum.



Fig. S2. Characterizations of Si nano-particles. (a) SEM image. (b) Number cumulative fractions for Si-particle size distributions. (c) Nitrogen adsorption linear plot. (d) XRD pattern. (e) Raman spectrum. (f) XPS spectrum.



Fig. S3. Schema of synthesis of the WPU.



Fig. S4. Long-term cycling performance of Si/C electrodes with different binders at 0.2C (1C=650 mAh g^{-1}).



Fig. S5. FT-IR spectra of the IPDI and WPU.



Fig. S6. ¹H-NMR of WPU (400 MHz, D₂O, 25 °C).



Fig. S7. The contact angle of (a) water, (b) CMC-Na, (c) WPU, and (d) CW-20 with carbon black.



Fig. S8. Stress-strain plots of (a) PVDF and (b) WPU films.



Fig. S9. XPS spectrum of (a) Si particles and (b) Si@CW-20 electrode.



Fig. S10. Characterizations of Si nano-particles. (a) and (b) TEM images at different magnifications. (c) HAADF image. (d-f) EDS mapping.



Fig. S11. CV curves of (a) CMC-Na and (b) CW-20 binders at a scan rate of 0.2 mV/s between 0.01 and 2.0 V.



Fig. S12. CV curves of (a) Si@PVDF, (b) Si@CMC-Na, and (c) Si@CW-20 electrodes at a scan rate of 0.1 mV/s between 0.01 and 1.2 V.



Fig. S13. Charge/discharge curves of (a) Si@PVDF, (b) Si@CMC-Na, and (c) Si@CW-20 electrodes at different C-rates.



Fig. S14. Charge-discharge curves of Si@CW-20 anodes with a limited specific capacity of 1000 mAh g^{-1} in Fig. 5f.



Fig. S15. High-rate performance of Si electrodes with different binders.



Fig. S16. (a) Nyquist plots of Si electrodes before cycling. (b) The analog circuit-1 for Nyquist plots before cycling. (c) R_0 and R_{CT} of Si electrodes before cycling. (d) Nyquist plots of Si electrodes after cycling. (e) The analog circuit-2 for Nyquist plots after cycling. (f) R_0 , R_{SEI} , and R_{CT} for Si electrodes after cycling.



Fig. S17. Morphology characterization of Si electrodes. TEM images of Si@CMC-Na (a) before and (b-c) after 200 cycles, and Si@CW-20 (d) before and (e-f) after 200 cycles.



Fig. S18. (a) The analog circuit-1 for Nyquist plots of Si/C electrodes before

cycling in Fig.7a. (b) The analog circuit-2 for Nyquist plots of Si/C electrodes after cycling in Fig.7d.

Table S1 Molecular weight and viscosity of WPU sample. The molecular weight of waterborne polyurethane was tested using a gel permeation chromatography device (1515, Waters). The flushing agent was tetrahydrofuran (THF) and the rinsing rate was 1 mL min^{-1} . The detector temperature was set to 35 °C and the column temperature was 35 °C.

	Molecula	ar weight	Vienneiter / (mBr. g. 25%C)
WPU	M_n	M_W	viscosity / (mPa·s, 25·C)
1	35,974	62,452	148
2	36,145	63,874	160
3	35,811	61,457	140
AVERAGR	35,976	62,594	149

	Li ₂ CO ₃	C=O(C-F)	C-O(C-N)	C-C	Total
Si@PVDF	23.92%	11.84%	12.59%	51.65%	100%
Si@CMC-Na	22.23%	11.10%	23.24%	43.42%	100%
Si@CW-20	15.03%	16.09%	11.97%	56.91%	100%

Table S2 The peak area compositions of C 1s spectrum.

1	LixPFyOz	LiF	C-F	Total
Si@PVDF	36.54%	28.79%	34.67%	100%
Si@CMC-Na	50.17%	49.83%	/	100%
Si@CW-20	/	100%	/	100%

Table S3 The peak area compositions of F 1s spectrum.