Electronic Supplementary Material (ESI) for Nanoscale Advances.
This journal is © The Royal Society of Chemistry 2023

Electronic Supplementary Information

In situ preparation of double gradient gradient anode materials based on polysiloxanefor lithium-ion batteries

Siqi Guan[a], Chen Xu[a], Yuanjiang Chen[a], Yongjin Zhang[a], Lixiang Li[a], b, Han Zhang[a], Baigang An[a, b*], Haiming Yang[a,b], Weimin Zhou[a,b], Chengguo Sun[a, c], Dongying Ju[b], and Xin Geng[a, b**]

[a] Institute of Energy Materials and Electrochemistry Research, University of Science and Technology Liaoning, Anshan 114051, PR China.
[b] Hainan Provincial Key Lab of Fine Chemistry, School of Chemical Engineering and Technology, Hainan University, Haikou 570228, China .
[c] School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

* Corresponding author.
** Corresponding authors at: Key Laboratory of Energy Materials and Electrochemistry Research Liaoning Province, School of Chemical Engineering, University of Science and Technology Liaoning, Anshan 114051, China.

E-mail: gengxin60@163.com(X. Geng), bgan@ustl.edu.cn (B. An). ;

Siqi Guan: Investigation, Conceptualization, Data curation, Methodology, Project administration, Formal analysis, Writing – original draft.
Chen Xu: Conceptualization, Methodology, Physicochemical characterization.
Yuanjiang Chen: Data curation, Formal analysis.
Yongjin Zhang: Data curation, Formal analysis.
Lixiang Li: Project administration, Writing – review & editing, Formal analysis.
Han Zhang: Methodology, Formal analysis. Haiming Yang: Formal analysis.
Baigang An: Supervision,Project administration, Data curation, Writing – review & editing.
Haiming Yang: Formal analysis.
Weimin Zhou: Formal analysis.
Chengguo Sun: Formal analysis.
Dongying Ju: Methodology, Formal analysis.
Xin Geng: Supervision, Project administration, Methodology, Writing – review & editing.

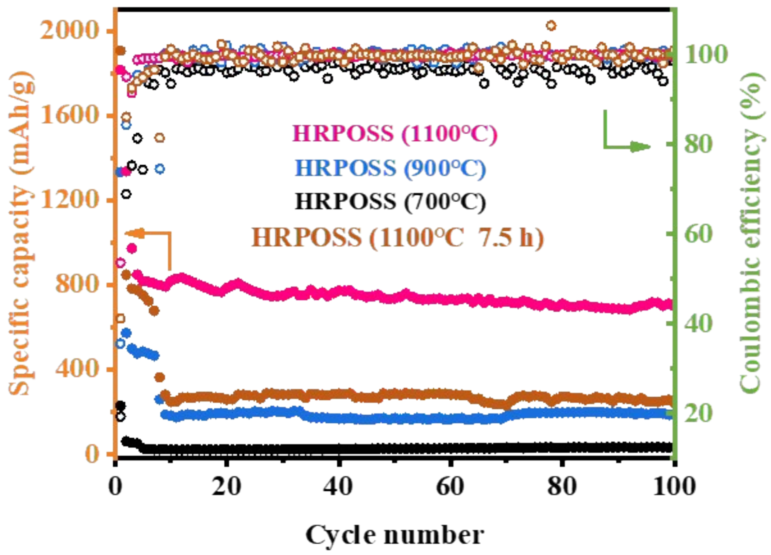

Fig. S1 Cycling curves of HRPOSS (700 ºC, 900 ºC, 1100 ºC and 1100 ºC-7.5 h) at a current density of 0.5 A g^{-1}.

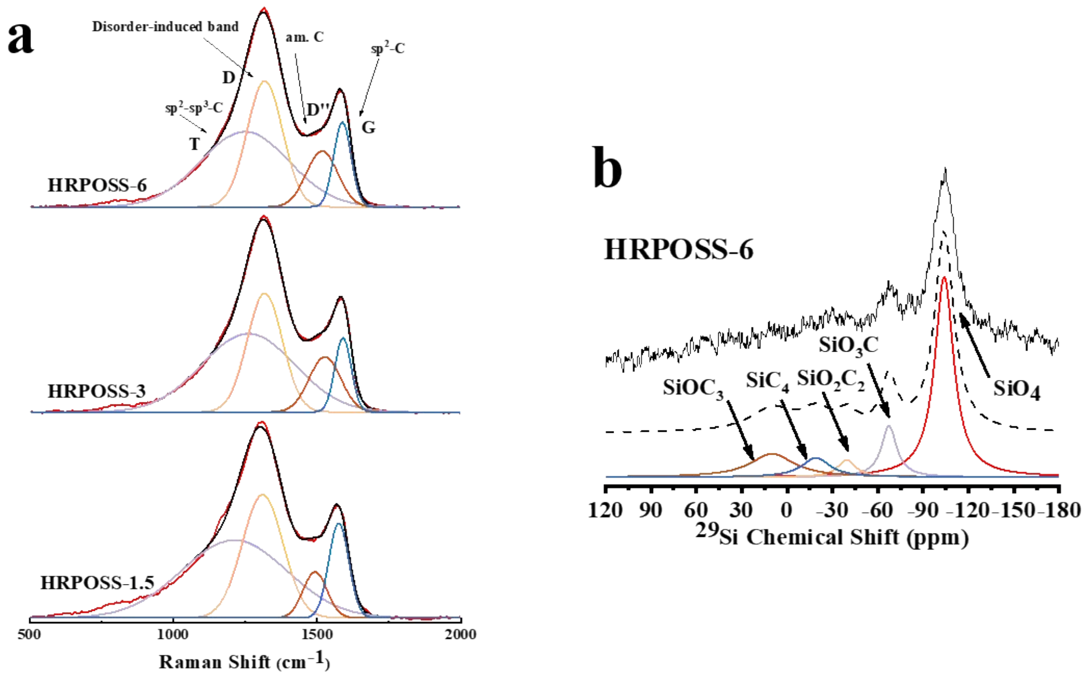

Fig. S2 (a) The characteristic carbon Raman and their definition, (b) ^{29}Si MAS-NMR spectra of HRPOSS-6. The experimental spectrum is shown by the bold curve on top, followed by the simulated spectrum (dashed curve), and the individual simulated components (bottom: solid curves).

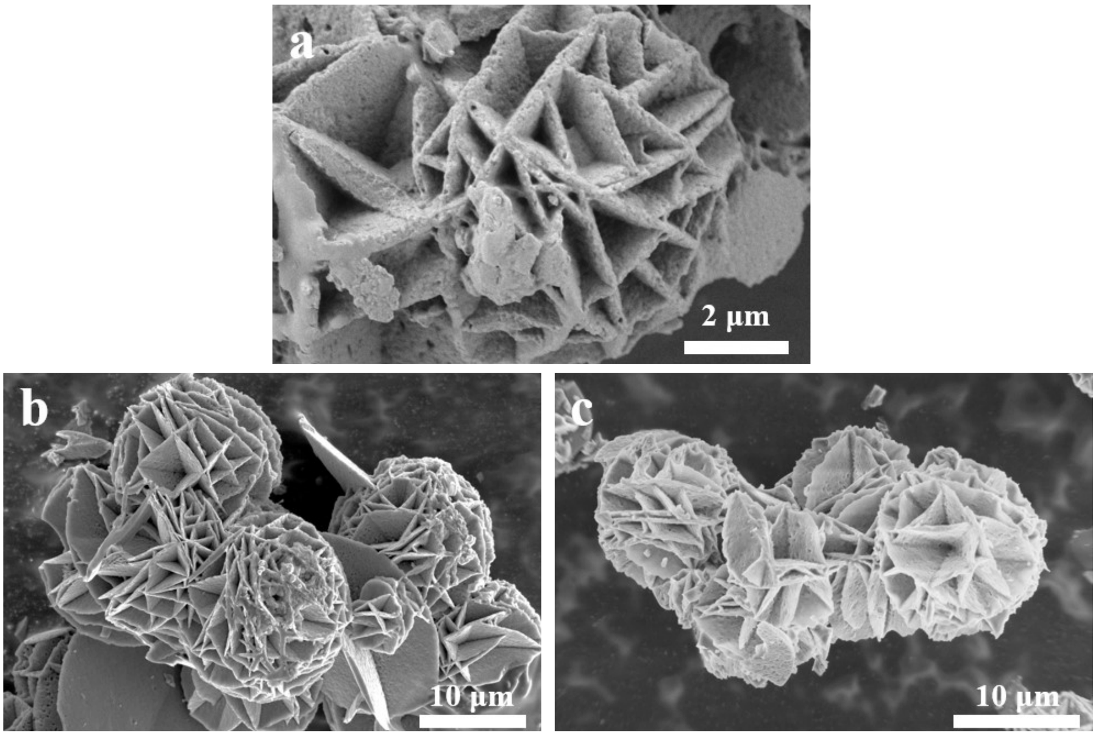

Fig. S3 SEM images of (a) POSS, (b) HRPOSS-1.5, (c) HRPOSS-3.

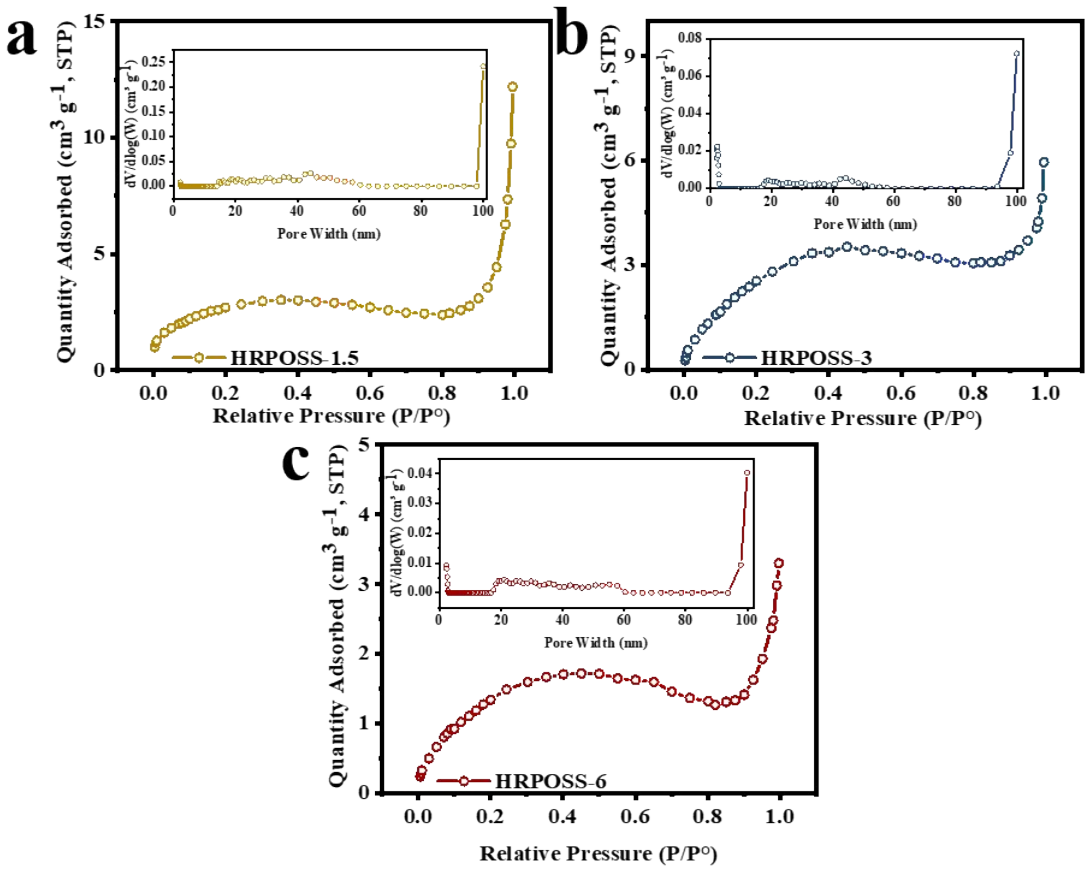

Fig. S4 Nitrogen adsorption-desorption isotherms and pore size distribution of (a) HRPOSS-1.5, (b) HRPOSS-3, (c) HRPOSS-6.

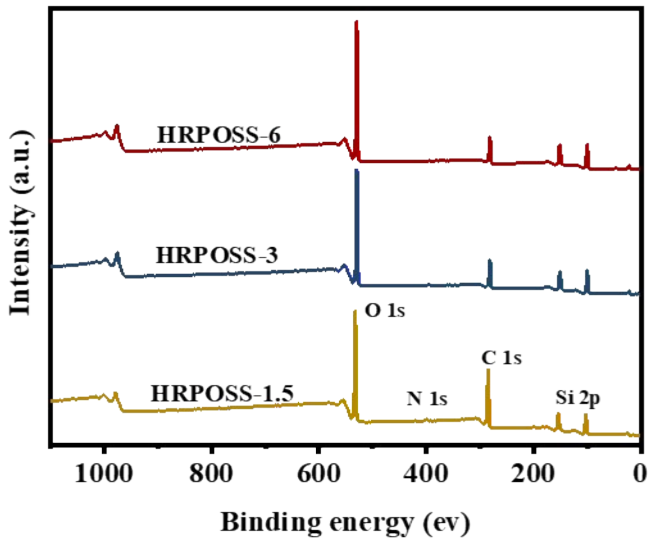

Fig. S5 XPS survey spectrum on the surface.

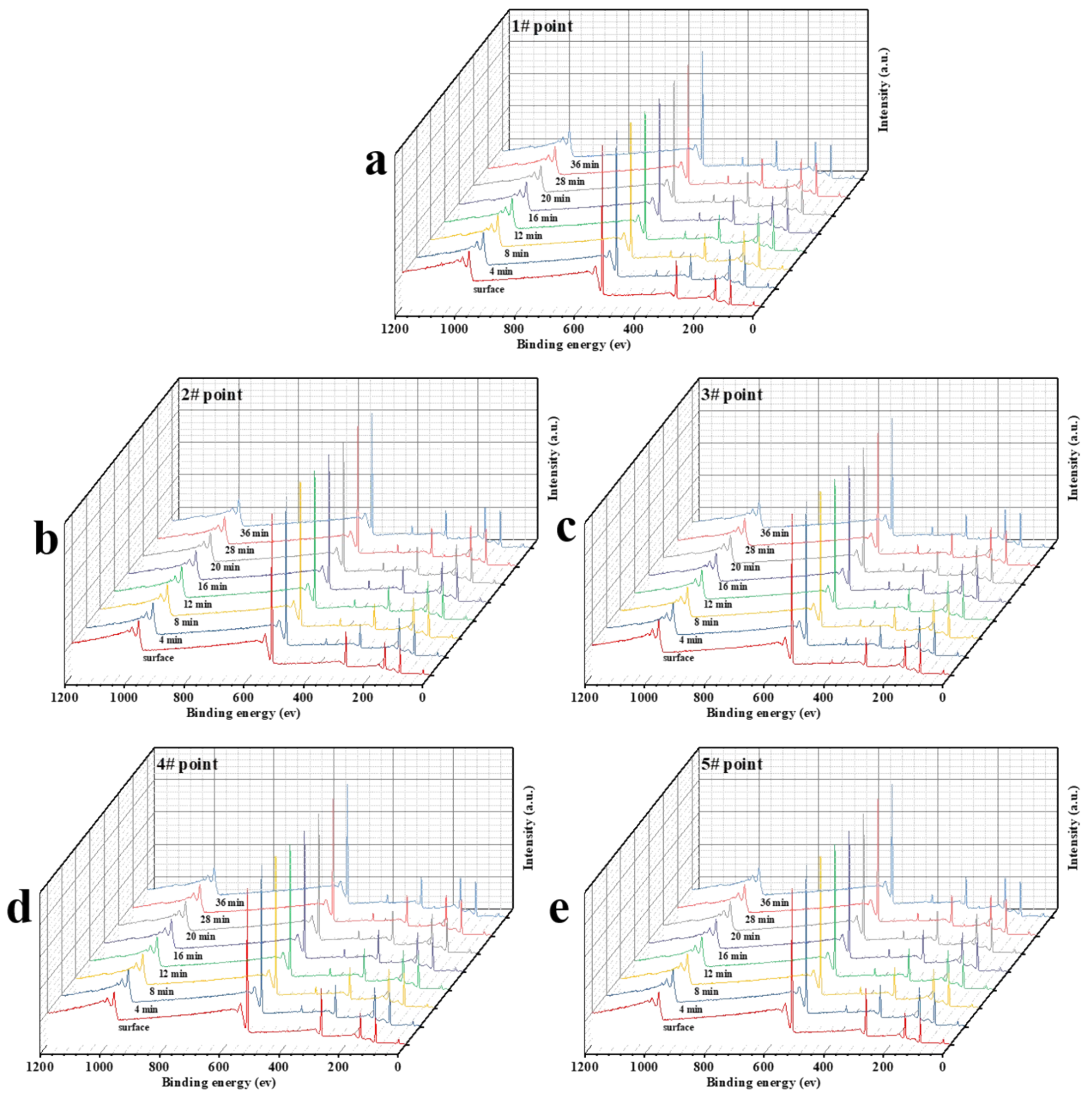

Fig. S6 XPS survey scan of HRPOSS-6 surface and after etching at 4 min intervals with Ar-ions sputtering at 5 keV (Five sites were randomly selected in a sample test range).

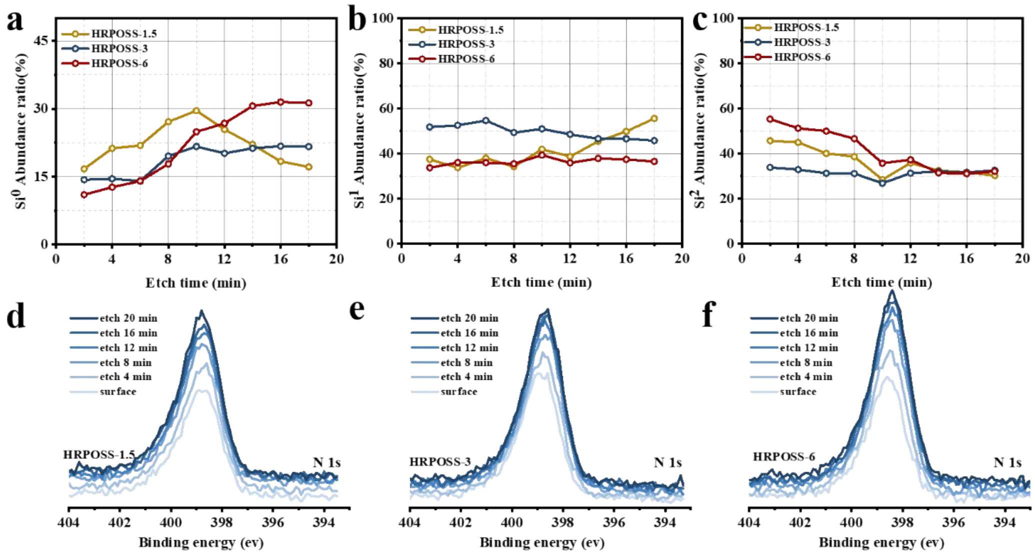

Fig. S7 Si high resolution spectrum fitting relative chemical state components (a) Si^{0+}, (b) Si^{1+}, (c) Si^{2+} and (d-f) N 1s region of the HRPOSS composites with Ar-ion sputtering.

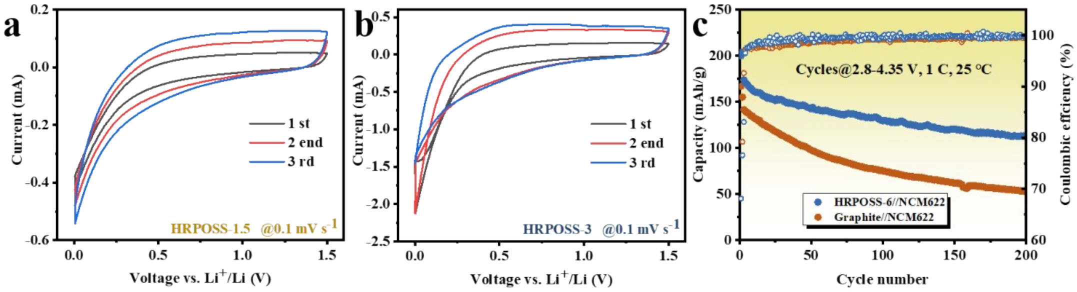

Fig. S8 (a,b) CV curves of HRPOSS-1.5 and HRPOSS-3, (c) Cycling performance of the Graphite//NCM622 full-cell and the HRPOSS-6//NCM622 full-cell.

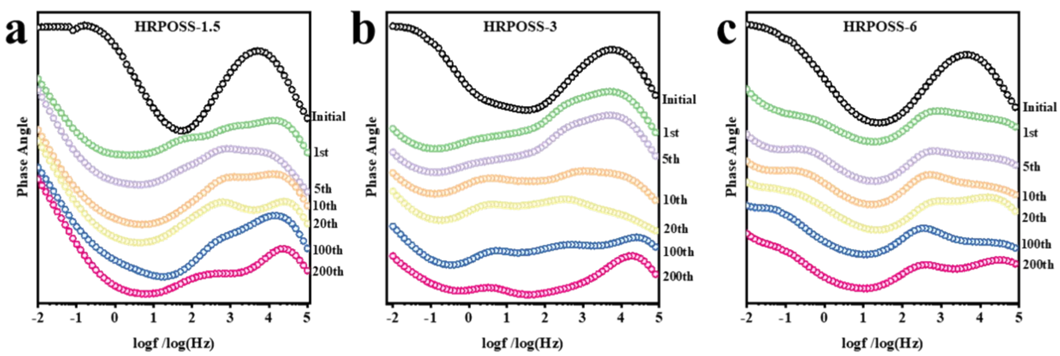

Fig. S9 (a-c) Bode plot of HRPOSS-1.5, HRPOSS-3 and HRPOSS-6 after various cycles.

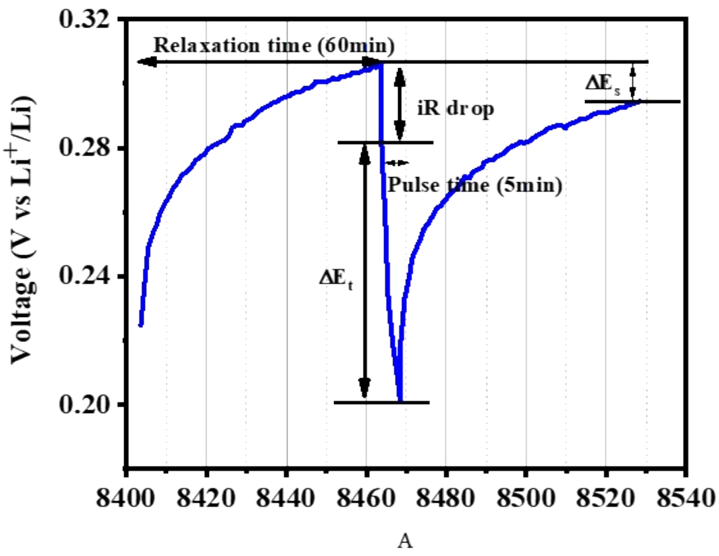

Fig. S10 E vs. t curves of HRPOSS electrode for a single GITT during discharge process.

The lithium diffusion coefficient was measured by using Galvanostatic Intermittent Titration Technique (GITT) and calculated based on Eq. (S1) as follows:

$$D_{Li^+} = \frac{4}{\pi\tau}\left(\frac{m_B V_M}{M_B S}\right)\left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2$$

Where τ is the relaxation time (s), and ΔE_s is the steady-state potential change (V) by the current pulse. ΔE_t is the potential change (V) during the constant current pulse after eliminating the iR drop. S is the electrode area and V_M is the molar volume.

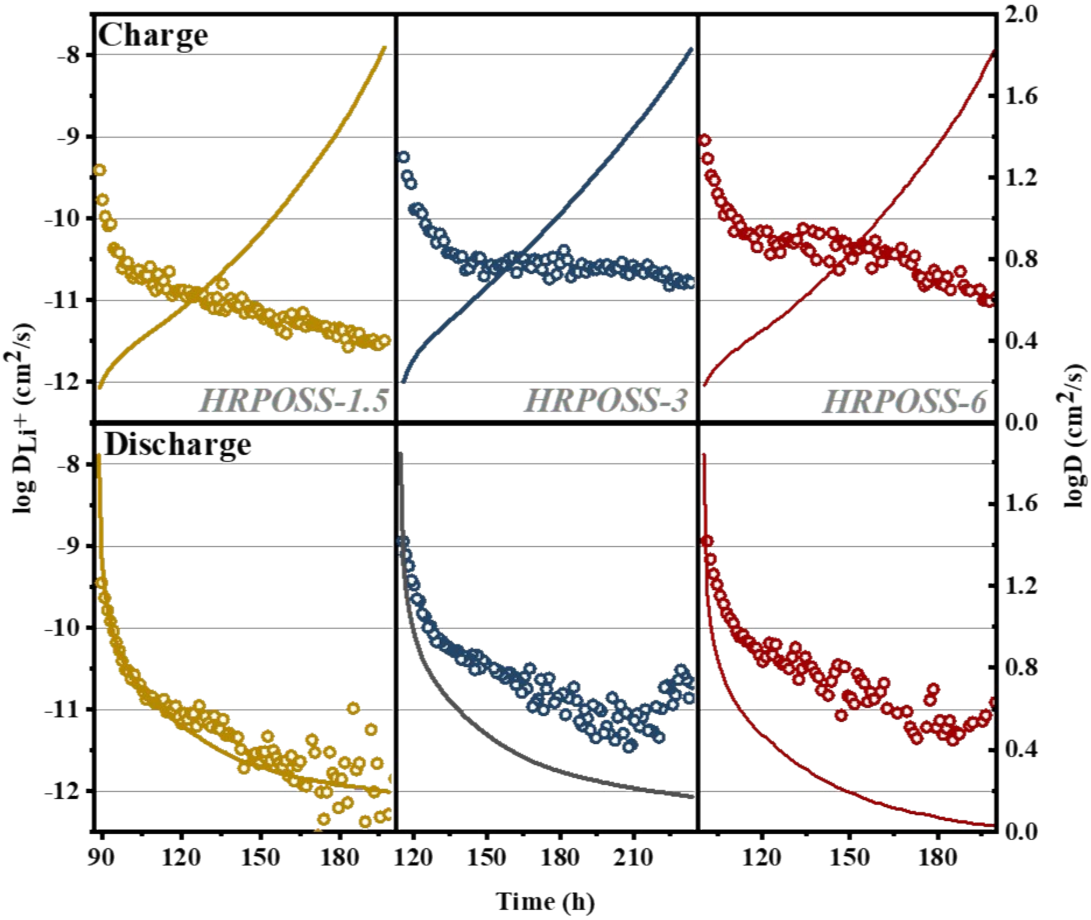

Fig. S11 GITT curves and the corresponding Li^+ diffusion coefficient at different discharge/charge state of electrodes.

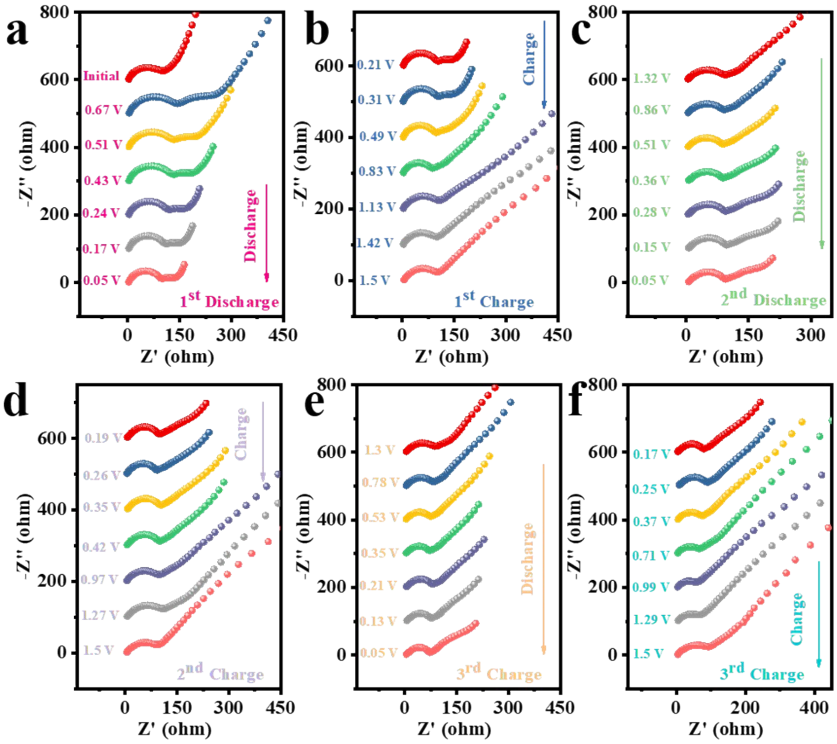

Fig. S12 Nyquist plots at different discharge/charge state of HRPOSS-6 electrode. (a) 1st discharge process, (b) 1st charge process, (c) 2nd discharge process, (d) 2nd charge process, (e) 3rd discharge process, (d) 3rd charge process.

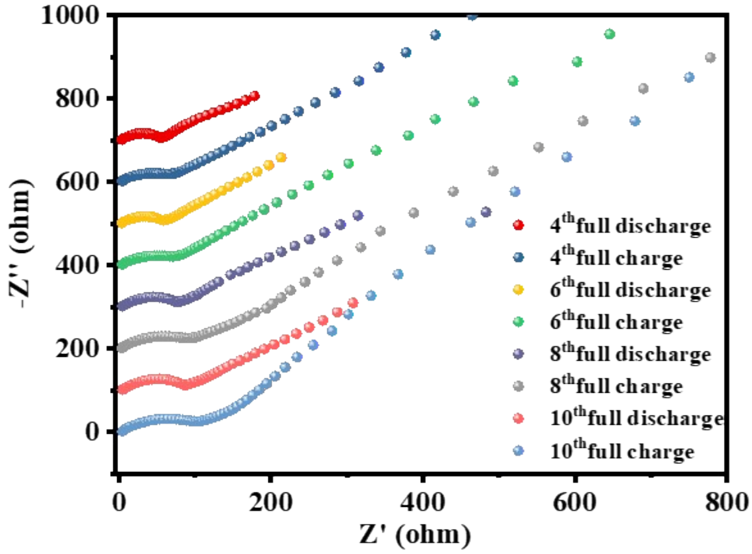

Fig. S13 Nyquist plots of fully discharged/charged states.

Table S1 The specific surface area and tapping density parameters

Samples	S_{BET}/m^2 g^{-1}	S_{micro}/m^2 g^{-1}	Tapping density/cm^3 g^{-1}
POSS	13.22	2.87	-
HRPOSS-1.5	10.09	2.72	0.62
HRPOSS-3	11.85	3.02	0.5
HRPOSS-6	5.06	0.45	0.8

Table S2 Percentage of average valence of Si in HRPOSS.

Samples	Average valence of Si		
	HRPOSS-1.5	HRPOSS-3	HRPOSS-6
(XPS, Sputtering t=0 min)	+1.30	+1.22	+1.50
(XPS, Sputtering t=2 min)	+1.29	+1.20	+1.44
(XPS, Sputtering t=4 min)	+1.24	+1.18	+1.39
(XPS, Sputtering t=6 min)	+1.18	+1.17	+1.36
(XPS, Sputtering t=8 min)	+1.12	+1.12	+1.29
(XPS, Sputtering t=10 min)	+0.99	+1.05	+1.12
(XPS, Sputtering t=12 min)	+1.10	+1.11	+1.10
(XPS, Sputtering t=14 min)	+1.10	+1.108	+1.01
(XPS, Sputtering t=16 min)	+1.13	+1.10	+1.00
(XPS, Sputtering t=18 min)	+1.16	+1.11	+1.01

Table S3 Composition of HRPOSS-6 measured by XPS

Samples(1# site)	Atomic Concentrations (%)			
	Si	N	C	O
(XPS, Sputtering t=0 min)	21.8	1.32	30.6	46.28
(XPS, Sputtering t=4 min)	29.1	3.65	22.3	44.95
(XPS, Sputtering t=8 min)	28.9	4.2	24.3	42.6
(XPS, Sputtering t=12 min)	29.43	4.7	25.11	40.76
(XPS, Sputtering t=16 min)	29.46	4.8	26.04	39.7
(XPS, Sputtering t=28 min)	28.97	4.37	27.2	39.46
(XPS, Sputtering t=36 min)	29.97	4.84	26.9	38.29

Samples(2# site)	Atomic Concentrations (%)			
	Si	N	C	O
(XPS, Sputtering t=0 min)	22.23	1.04	29.49	47.24
(XPS, Sputtering t=4 min)	29.76	3.9	20.55	45.79
(XPS, Sputtering t=8 min)	29.95	4.48	22.39	43.18
(XPS, Sputtering t=12 min)	30.42	4.47	23.26	41.85
(XPS, Sputtering t=16 min)	30.3	5.04	23.52	41.14
(XPS, Sputtering t=28 min)	30.27	4.77	25.06	39.9
(XPS, Sputtering t=36 min)	31.41	5.12	24.72	38.75

Samples(3# site)	Atomic Concentrations (%)			
	Si	N	C	O
(XPS, Sputtering t=0 min)	25.92	1.38	24.8	47.9
(XPS, Sputtering t=4 min)	30.69	3.52	19.92	45.87
(XPS, Sputtering t=8 min)	31.37	4.39	21.33	42.91
(XPS, Sputtering t=12 min)	31.2	4.97	22.47	41.36
(XPS, Sputtering t=16 min)	31.74	5.15	22.07	41.04
(XPS, Sputtering t=28 min)	31.05	5.09	23.9	39.96
(XPS, Sputtering t=36 min)	31.89	5.53	23.45	39.13

Samples(4# site)	Atomic Concentrations (%)			
	Si	N	C	O
(XPS, Sputtering t=0 min)	20.44	1.13	35.42	43.01
(XPS, Sputtering t=4 min)	27.24	3.74	26.79	42.23
(XPS, Sputtering t=8 min)	28.11	4.16	26.64	41.09
(XPS, Sputtering t=12 min)	28.61	4.65	26.95	39.79
(XPS, Sputtering t=16 min)	28.89	4.82	27.42	38.87
(XPS, Sputtering t=28 min)	28.9	4.83	28.09	38.18
(XPS, Sputtering t=36 min)	30.02	5.1	27.25	37.63

Samples(5# site)	Atomic Concentrations (%)			
	Si	N	C	O
(XPS, Sputtering t=0 min)	21.34	1.22	35.2	42.24
(XPS, Sputtering t=4 min)	28.57	4.16	24.63	42.64
(XPS, Sputtering t=8 min)	29.24	4.49	25.32	40.95
(XPS, Sputtering t=12 min)	29.87	4.59	25.7	39.84
(XPS, Sputtering t=16 min)	29.33	4.86	26.38	39.43
(XPS, Sputtering t=28 min)	29.84	5.23	26.22	38.71
(XPS, Sputtering t=36 min)	30.96	5.41	25.45	38.18