

**A composite electrolyte based on aluminum oxide filler/polyester polymer
via in situ thermal polymerization for long-cycle sodium metal batteries**

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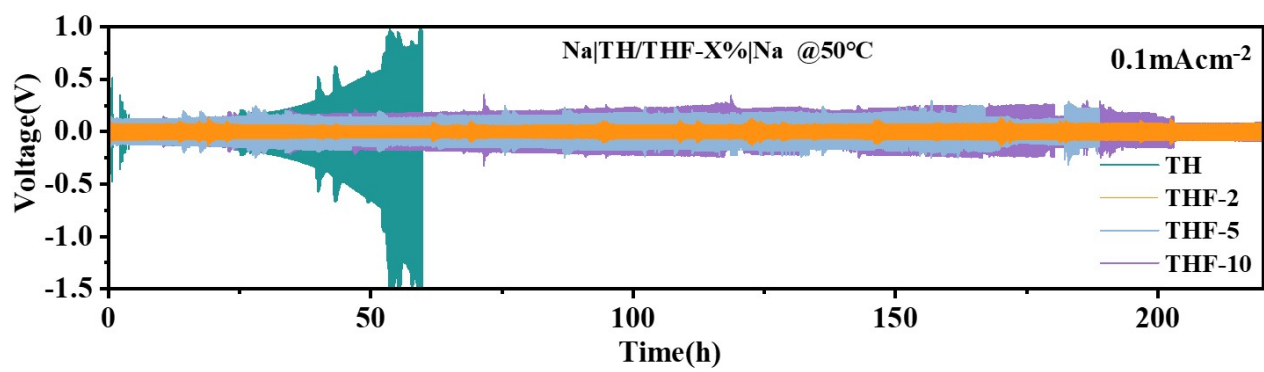


Figure S1. Electroplating stripping cycle performances of Na|TH|Na and Na|THF-X|Na cells at 0.1 mA cm^{-2} .

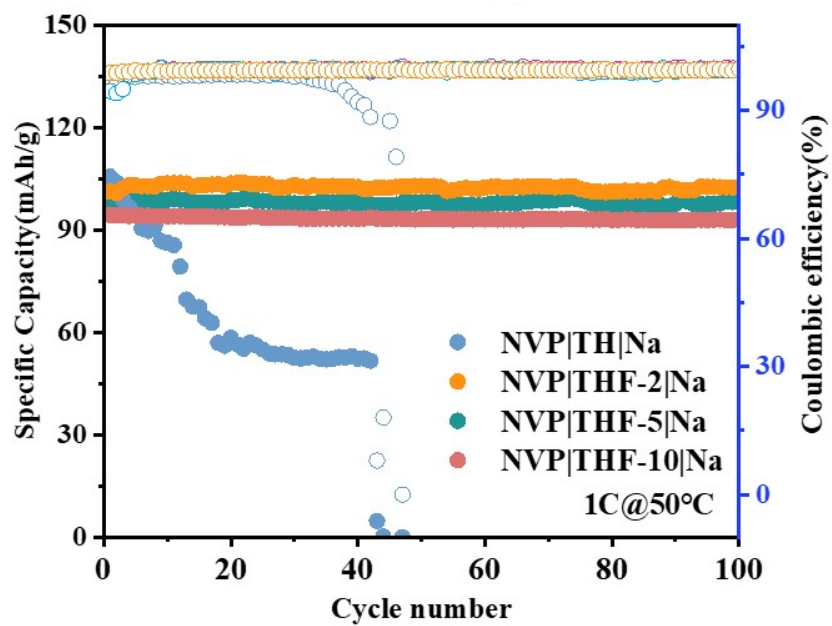


Figure S2. Long cycling performance of NVP|TH|Na and NVP|THF-X|Na cells at 1 C and 50 °C.

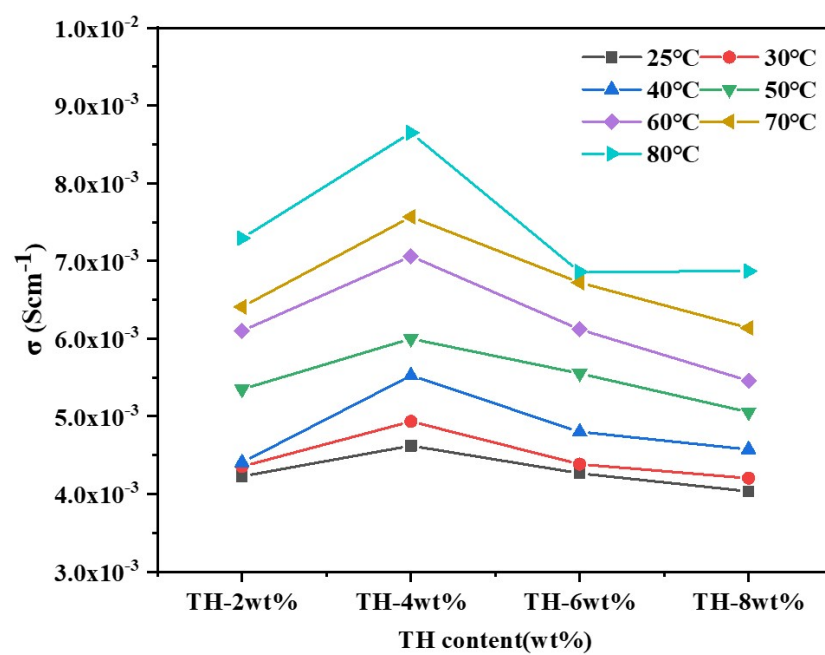


Figure. S3 Arrhenius plot of TH-2wt%, TH-4wt%, TH-6wt%, and TH-8wt%.

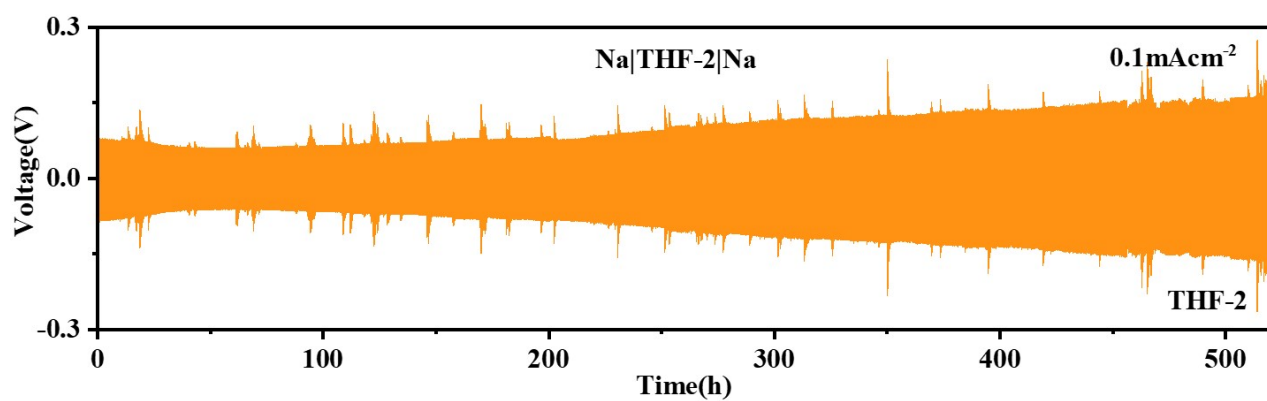


Figure S4. Electroplating stripping cycle performance of Na|THF-2|Na cell at 0.1 mA cm⁻².

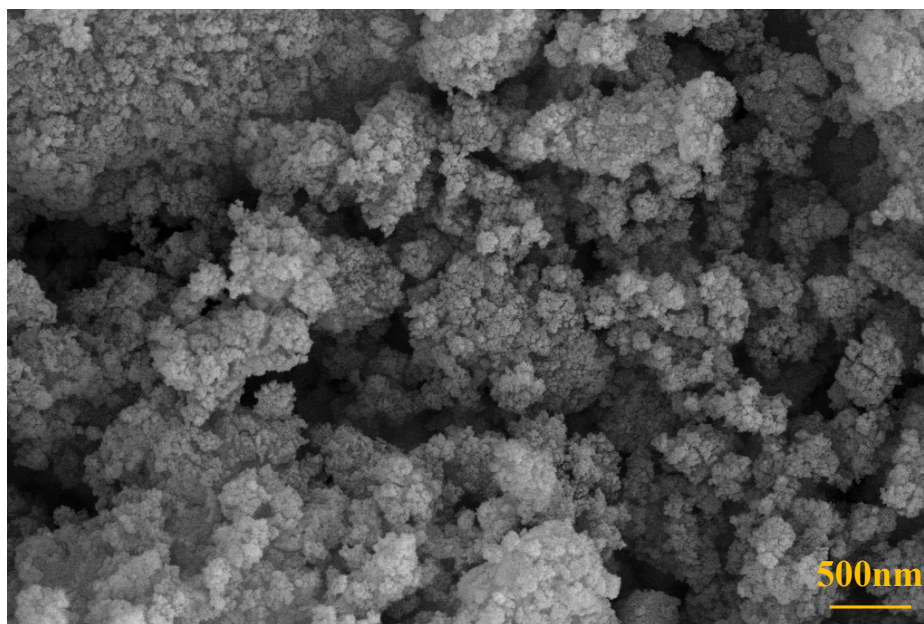


Figure. S5 SEM image of Al₂O₃ filler.

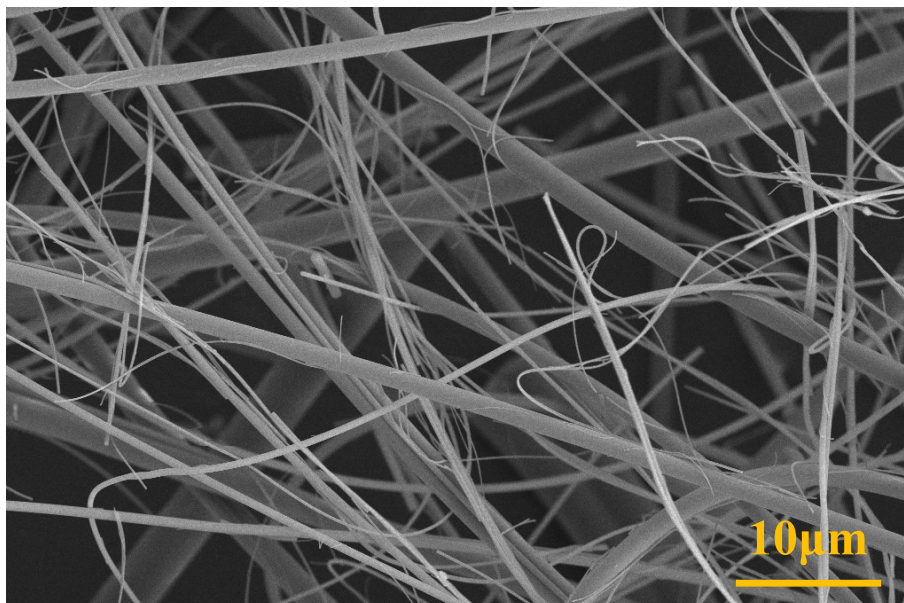


Figure S6. SEM images of blank glass fiber membrane.

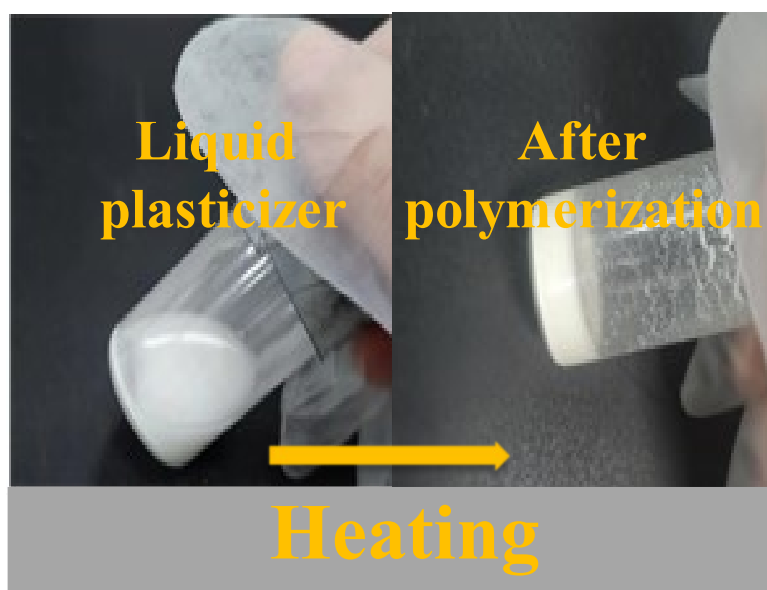


Figure S7. In situ thermal polymerization process of THFA-5 electrolyte.

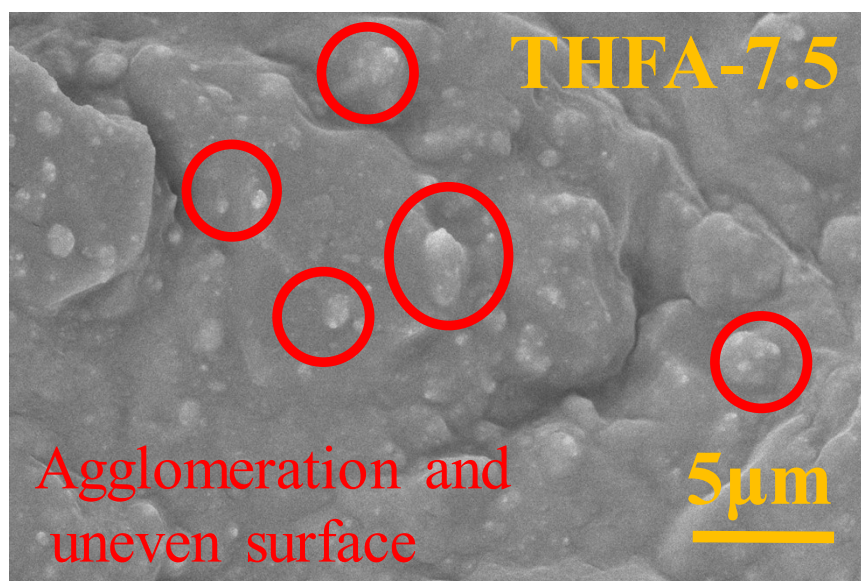


Figure S8. SEM images of THFA-7.5 electrolyte.

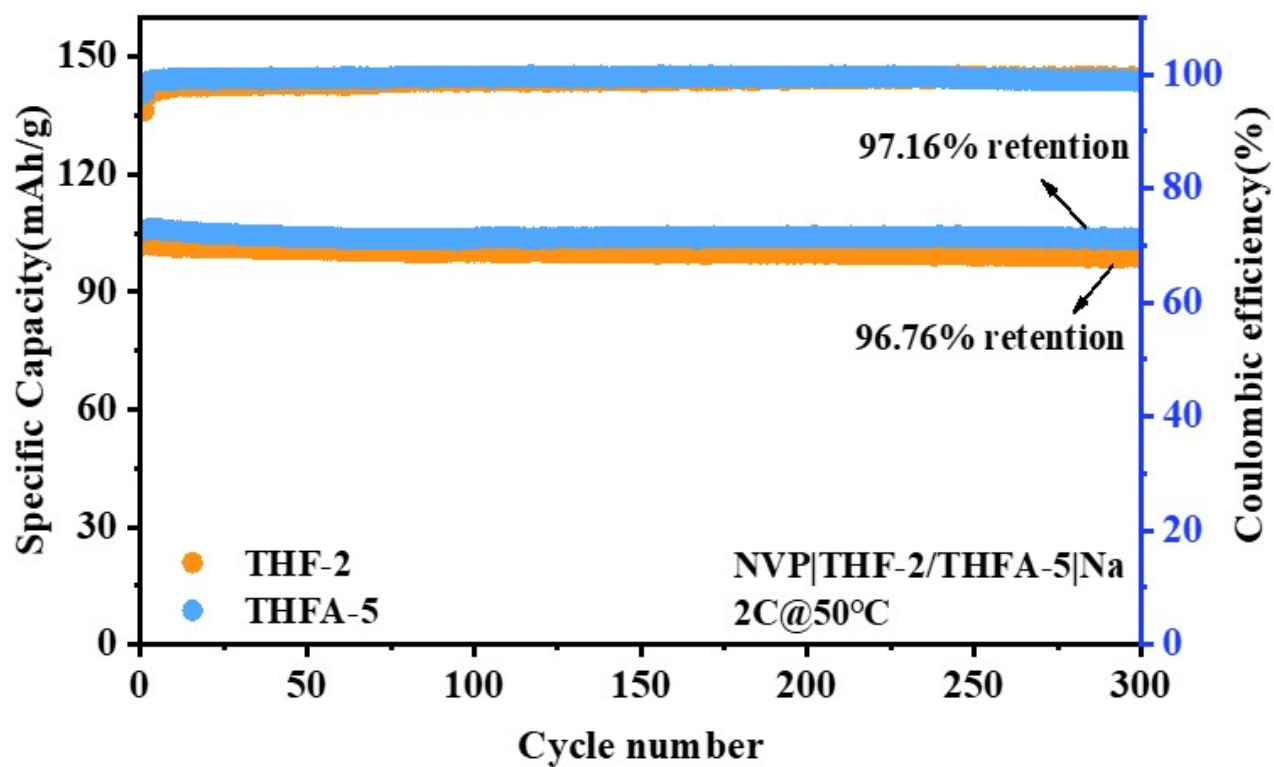


Figure S9. Long cycling performance of NVP|THF-2|Na and NVP|THFA-5|Na cells.

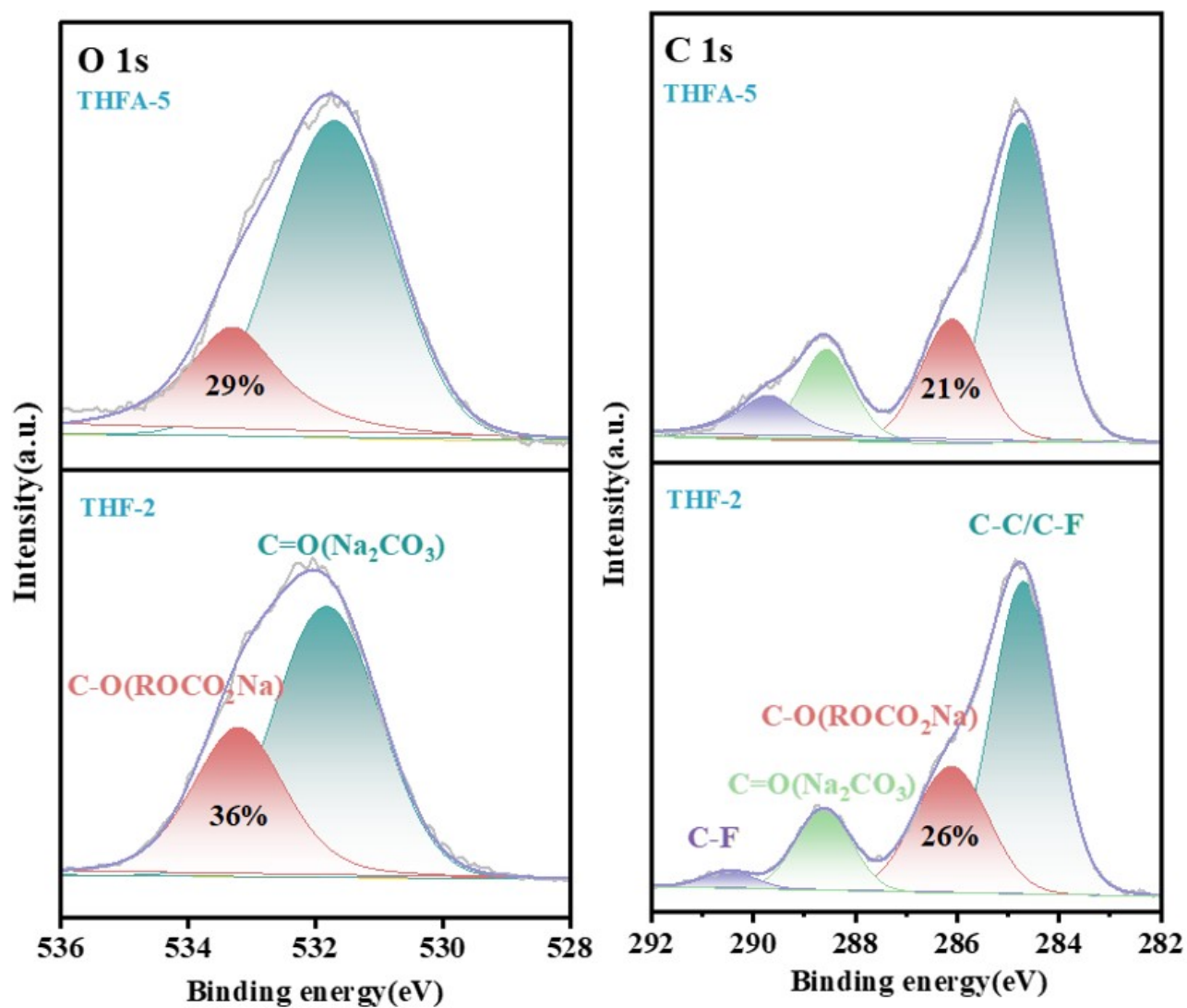


Figure S10. O 1s and C 1s of XPS spectra of cycled NVP with THFA-5 and THF-2 electrolytes.

Table. S1. Comparison of Ea of different electrolyte samples

Sample	THF-2	THFA-2.5	THFA-5	THFA-7.5
Ea (kJ·mol ⁻¹)	9.792	10.323	9.666	10.558
Ea (eV)	0.102	0.108	0.100	0.110

Table. S2. Electrochemical performance comparison of the NVP|THFA-5|Na cell with other recently reported NVP-based cells.

NVP-based cells	Rate performance (average capacity)	Cycling stability (capacity retention)	Ref.
NVP PEGMA-NaTFSI-TEP-FEC Na	0.2 C, 102 mA h g ⁻¹	400 cycles, 91%(0.2 C)	[1]
NVP DOL-TMPTGE-NaPF ₆ -PC-FEC Na	0.1 C, 90 mA h g ⁻¹	100 cycles, 96% (0.2 C)	[2]
NVP PBA-NaPF ₆ -EC-DEC Na	1 C, 90 mA h g ⁻¹	300 cycles, 83% (1 C)	[3]
NVP PEO-SN-NaClO ₄ NZSP-NSO Na	0.5 C, 105 mA h g ⁻¹	100 cycles, 95% (0.5 C)	[4]
NVP PEO-NaTFSI-BCOF Na	1 C, 82 mA h g ⁻¹	1200 cycles, 81.2% (1 C)	[5]
NVP DOL-NaTFSI-FEC-Al(OTf) ₃ Na	0.5 C, 107 mA h g ⁻¹	600 cycles, 96.7% (0.5 C)	[6]
NVP PEO-NaFSI-Al ₂ O ₃ -AQ Na	1 C, 90 mA h g ⁻¹	2000 cycles, 92.8% (1 C)	[7]
NVP NaClO ₄ -PEO-EC-DEC-FEC-NZSP Na	0.2 C, 78 mA h g ⁻¹	50 cycles, 93.5% (0.2 C)	[8]
NVP G-NASICON Na	1 C, 106 mA h g ⁻¹	300 cycles, 85% (1 C)	[9]
NVP ANs-PVdF-HFP-γ-Al ₂ O ₃ Na	1 C, 99.5 mA h g ⁻¹	500 cycles, 95.2% (1 C)	[10]
NVP PVDF-NaTFSI-NaDFOB Na	1 C, 109 mA h g ⁻¹	300 cycles, 89.8% (1 C)	[11]
NVP PEG-HCCP-NaClO ₄ -PEGDA-HCP-BDB Na	0.1 C, 93.8 mA h g ⁻¹	100 cycles, 91.4% (0.1 C)	[12]
NVP PEO-NaPF ₆ - Na	2 C, 84.9 mA h g ⁻¹	200 cycles, 85.8% (1 C)	[13]

NVP TMPTMA-HDDA- NaTFSI-DMC-PC-FEC- Al ₂ O ₃ Na	1 C,104.3 mA h g ⁻¹	1500 cycles, 97.79%(1 C)	This work
	2 C,102.2 mA h g ⁻¹	2000cycles,88.06%(2 C)	

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