Supplementary Materials

Insight and regulation of interfacial coordination chemistry of high-voltage $LiCoPO_4$ cathode via functionalized carbon layer anchoring for robust surface passivation

Moohyun Woo [a] and George P. Demopoulos [a*]

[1] Materials Engineering, McGill University, 3610 rue University, Montréal, QC H3A 0C5, Canadax

[*] Corresponding author: Prof. George P. Demopoulos, email: george.demopoulos@mcgill.ca; ORCID# https://orcid.org/ **0000-0001-8112-5339**

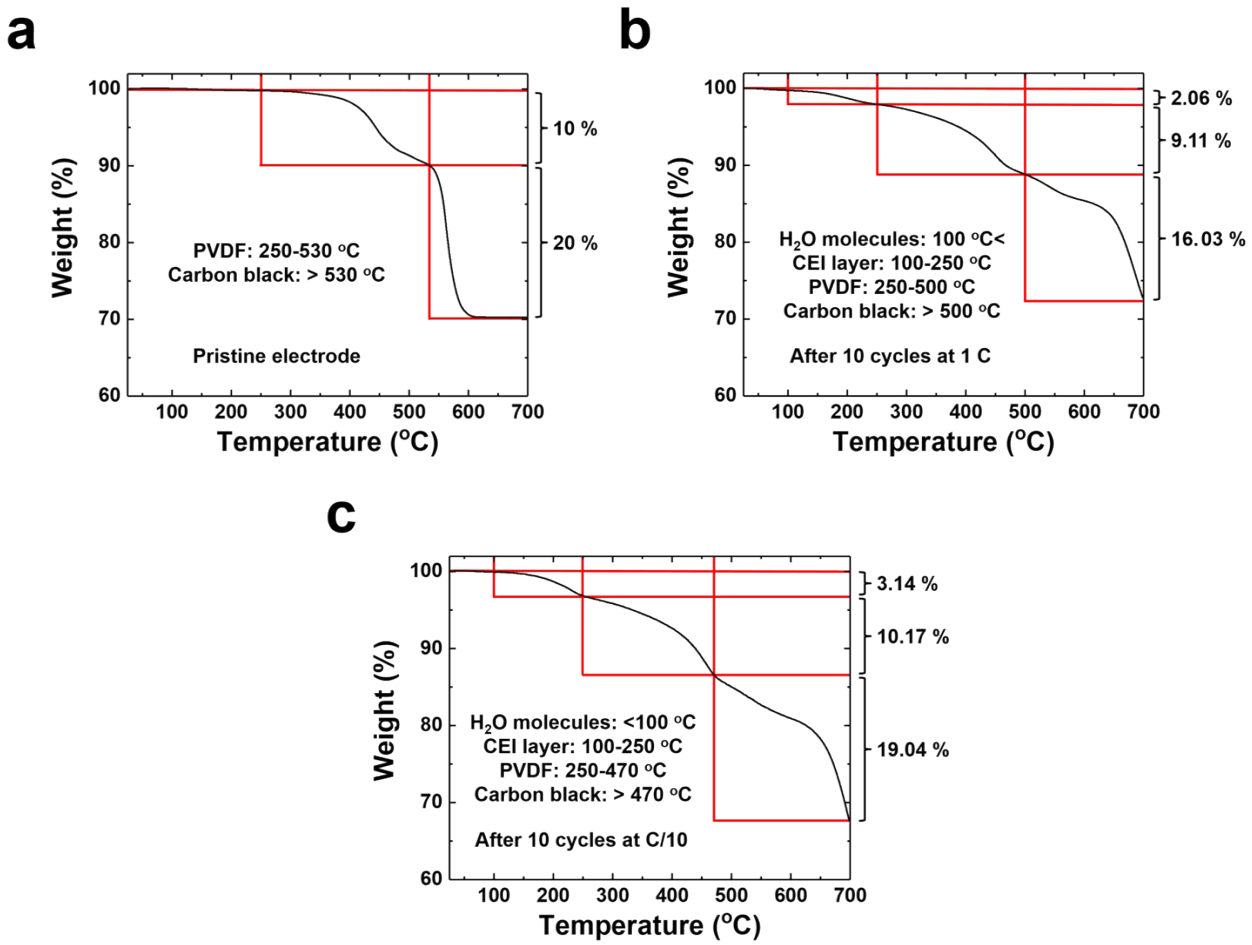

Figure S1. TGA curves of (a) pristine and cycled electrodes after 10 cycles at (b) 1 C and (c) C/10 over the whole temperature range up to 700 °C.

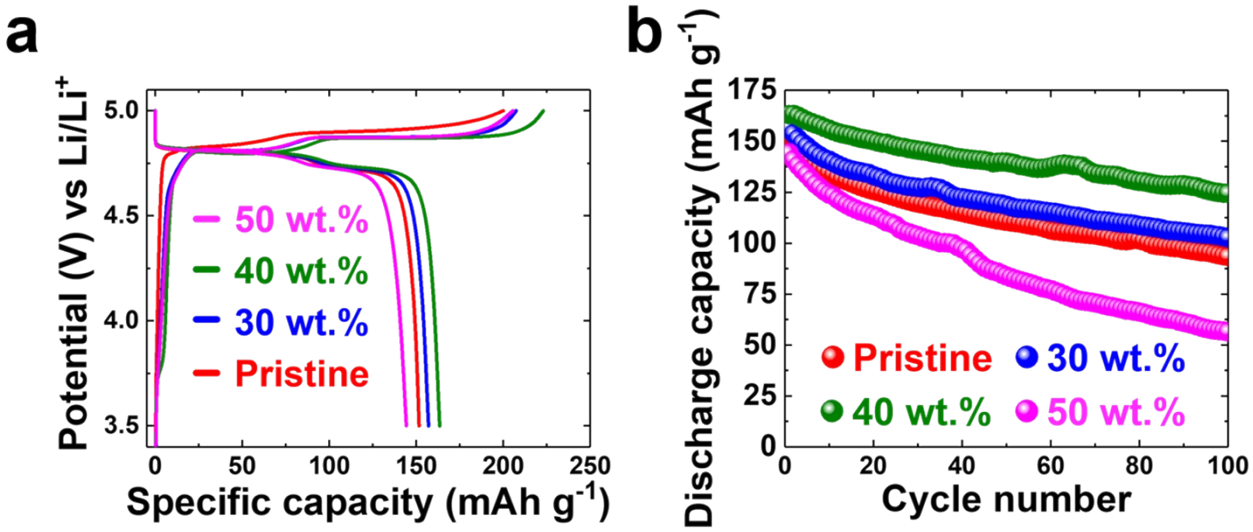

Figure S2. Electrochemical evaluations on the effect of functionalized carbon layer via (a) galvanostatic charge-discharging and (b) capacity retention with different amount of sucrose, measured within the voltage range 3.5-5.0 V vs. Li/Li^+ at 1 C.

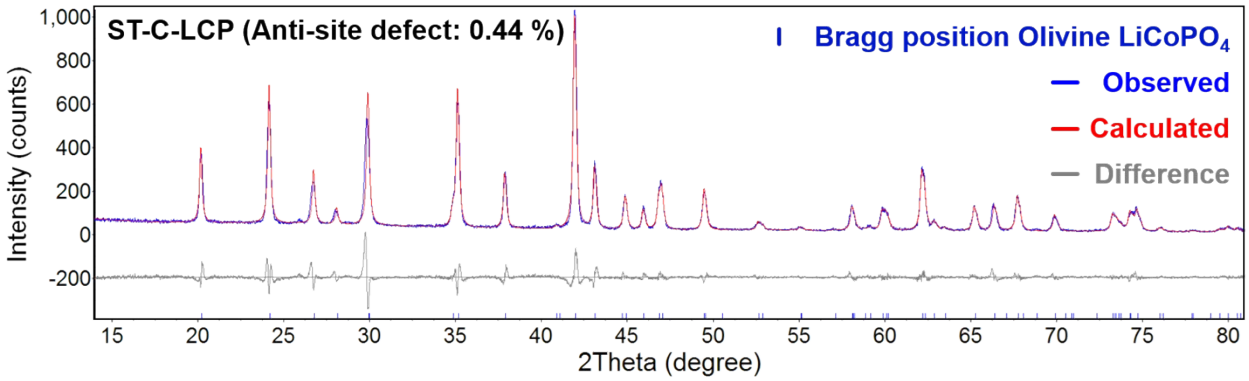

Figure S3. Rietveld refinement result of ST-C-LCP based on XRD pattern.

Table S1. Refined XRD data of ST-C-LCP.

ST-C-LCP	
a (Å)	10.19
b (Å)	5.92
c (Å)	4.70
Unit cell volume ($Å^3$)volume ($Å^3$)	283.53
Grain size (nm)	67.3
Anti-site defect concentration (%)	0.44
R_{wp} (%)	6.52

Peak	Bond	Binding energy (eV)	FWHM (eV)	Atomic %
C 1s	C=C & C-C	284.77	1.26	52.82
	C-OH	285.33	1.43	20.93
	C-O-C	286.53	1.31	9.18
	C=O	289.32	1.86	3.99
	COOH	291.17	3.51	6.20
	π- π	287.76	1.64	6.87
O 1s	P-O & C=O	531.23	1.02	4.20
	COOH	532.28	1.56	43.76
	C-OH	533.35	1.38	30.60
	C-O-C	534.20	1.81	21.43

Table S2. XPS peak data summary of as-synthesized ST-C-LCP powder.

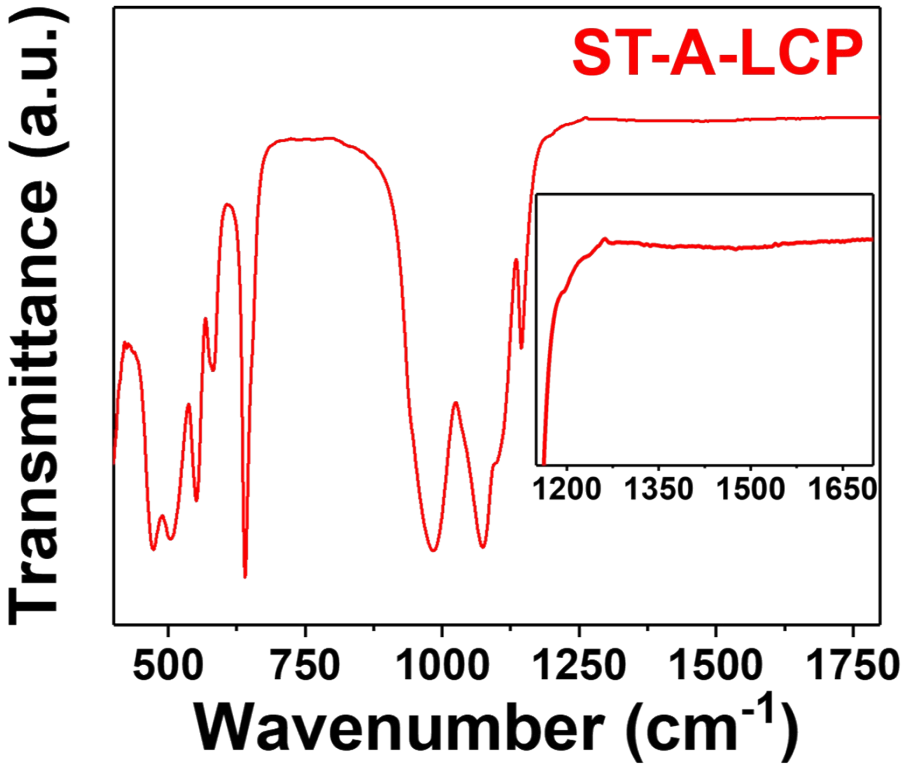

Figure S4. FT-IR spectrum of ST-A-LCP.

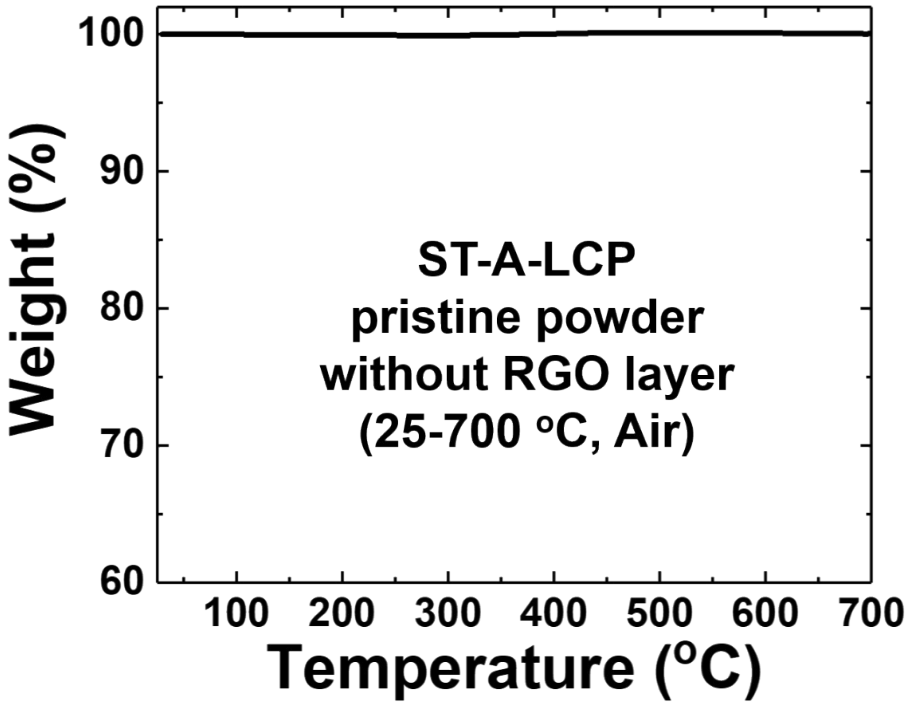

Figure S5. TGA curves of ST-A-LCP powder without FCL coating over the whole temperature range up to 700 °C in air.

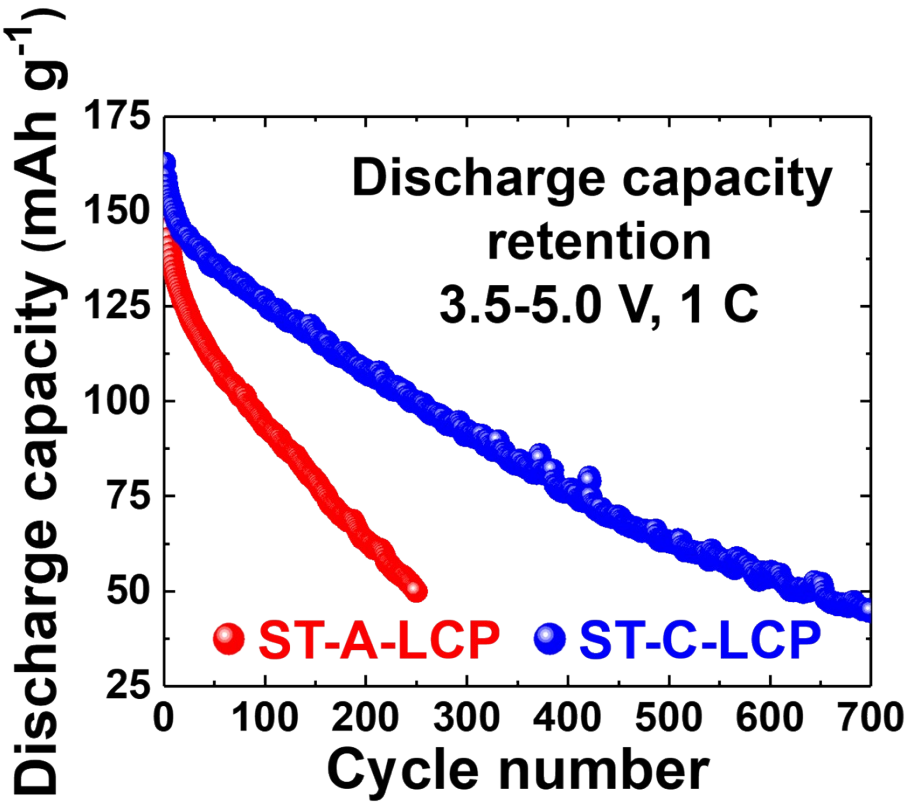

Figure S6. Comparison of discharge capacity retention of ST-A-LCP and ST-C-LCP at 1 C.

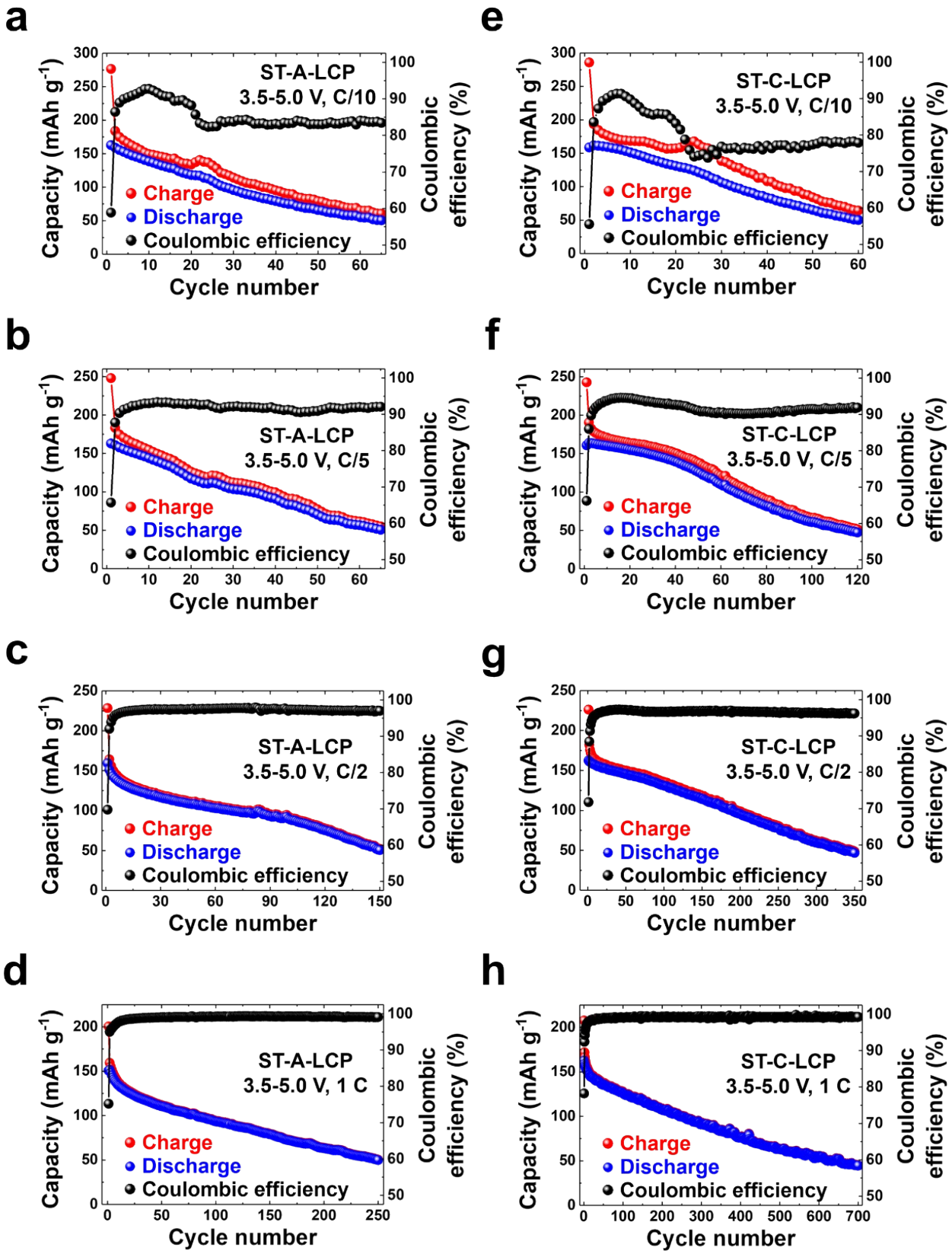

Figure S7. Capacity retention and Coulombic efficiency of ST-A-LCP and ST-C-LCP within the voltage range 3.5-5.0 V vs. Li/Li^+ at different C-rates.

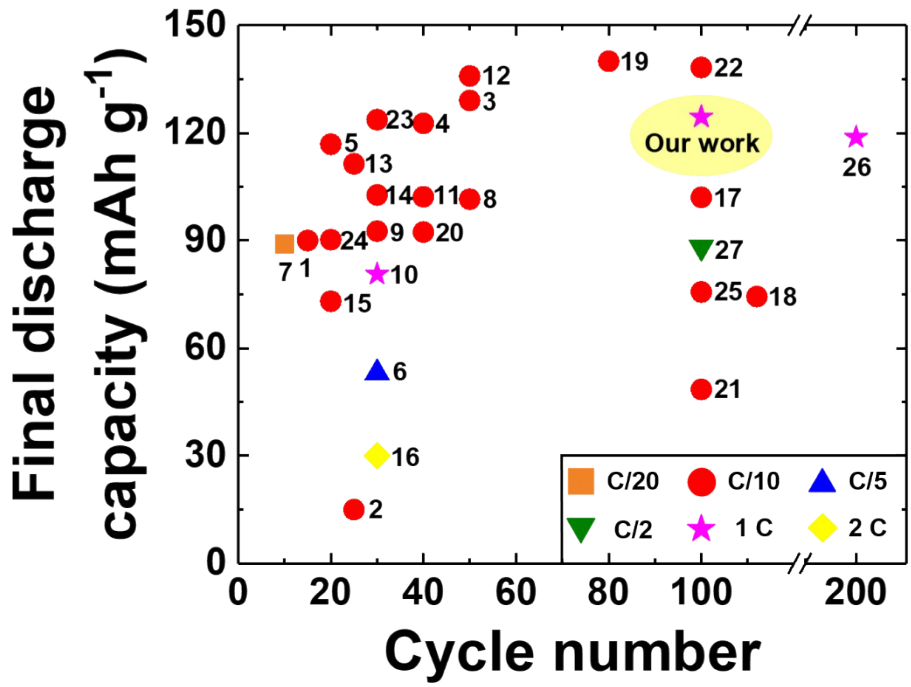

Figure S8. Comparative evaluation of final discharge capacity as a function of cycle number for ST-C-LCP and previously reported carbon-coated LCP systems at various C-rates.

Table S3. Comprehensive summary of experimental parameters for the surveyed carbon-coated LCP literatures.

Carbon source	Electrode composition (wt.%)	Electrolyte	Voltage range (V)	Initial discharge capacity (mAh g^{-1}) & C-rate	Capacity retention	Ref.
MWCNT	75:12.5:12.5 (AM:Carbon:TAB)	1 M $LiPF_6$ in EC/DEC = 1:1 (v/v)	3.5-5.0	120, C/10	75 % after 15 cycles	1
Glucose	75:12.5:12.5 (AM:Carbon:TAB)	1 M $LiPF_6$ in EC/DEC = 1:1 (v/v)	3.5-5.0	52, C/10	28.8 % after 25 cycles	2
Glucose	70:20:10 (AM:CB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	3.2-5.1	133, C/10	97 % after 50 cycles	3
AB	70:20:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	2.5-5.1	141, C/10	87 % after 40 cycles	4
Citric acid	85:10:5 (AM:CB:PVDF)	1 M $LiPF_6$ in EC/DEC = 1:1 (v/v) with 1 wt.% LiBOB	3.0-5.0	123, C/10	95 % after 20 cycles	5
Glucose	80:10:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	2.0-5.0	108, C/5	49.1 % after 30 cycles	6
PEDOT, MWCNT	83:10:7 (AM:AB:PTFE)	1 M $LiPF_6$ in EC/DEC = 1:1 (v/v)	3.5-5.0	130, C/20	68.5 % after 10 cycles	7
AB	80:12.5:7.5 (AM:CB:PVDF)	1 M $LiPF_6$ in EC/DEC = 1:1 (v/v)	3.0-5.0	145, C/10	70 % after 50 cycles	8
Citric acid	75:20:5 (AM:AB:PTEE)	1 M $LiPF_6$ in EC/DEC/EMC = 1:1:1 (v/v/v) with 0.1 wt.% TPN	3.5-5.2	136.2, C/10	68 % after 30 cycles	9
AB	70:20:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	2.5-5.0	128, 1 C	63 % after 30 cycles	10
Citric acid	80:10:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	3.0-5.2	131, C/10	78 % after 40 cycles	11
PVP	80:10:10 (AM:MWCNT: PVDF)	1 M $LiPF_6$ in EC/DEC = 1:1 (w/w)	3-5.1	153, C/10	88.8 % after 50 cycles	12

Kerosene, Heptane	70:20:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	2.5-5.1	128, C/10	87 % after 25 cycles	13
Propane	80:10:10 (AM:CB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	3.0-5.0	130, C/10	79 % after 30 cycles	14
Sucrose	80:10:10 (AM:AB:PTFE)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	3.0-5.1	130, C/10	56.2 % after 20 cycles	15
Ethylene glycol	90:5:5 (AM:CB:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	2.5-5.5	114, 2 C	26.3 % after 30 cycles	16
Sucrose	75:15:10 (AM:Super P: PVDF)	1 M $LiPF_6$ in FEC/DMC = 1:4 (v/v)	3.0-5.0	123.8, C/10	82.4 % after 100 cycles	17
Sucrose	85:10:5 (AM:Super C45:CMC)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	4.0-5.0	120, C/10	62 % after 112 cycles	18
Tannic acid	85:7:8 (AM:Super P: PVDF)	1 M $LiPF_3(CF_2CF_3)$ in EC/DMC = 1:1 (v/v)	2.6-5.2	155.2, C/10	90.2 % after 80 cycles	19
Sucrose, Graphene oxide	70:20:10 (AM:AB:PVDF)	1 M $LiPF_6$ in FEC/DMC = 1:1 (v/v)	3.0-5.3	146.1, C/10	63.2 % after 40 cycles	20
CMC	80:10:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DEC = 1:2 (v/v)	3.0-5.1	125.3, C/10	38.7 % after 100 cycles	21
Alginic acid	86:7:7 (AM:Super P: PVDF)	1 M $LiPF_3(CF_2CF_3)$ in EC/DMC = 1:1 (v/v)	2.8-5.2	160, C/10	86.4 % after 100 cycles	22
CMC	75:15:10 (AM:AB:PVDF)	1 M $LiPF_6$ in EC/DEC = 1:2 (v/v)	3.0-5.1	135, C/10	91.6 % after 30 cycles	23
Sucrose	80:10:10 (AM:Super P: PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	3.5-5.2	120.3, C/10	75 % after 20 cycles	24
CMC	80:10:10 (AM:Carbon: PVDF)	1 M $LiPF_6$ in EC/DEC = 1:2 (v/v)	3.0-5.3	133.7, C/10	56.6 % after 100 cycles	25

Sucrose, PVDF, CTAB	80:10:10 (AM:Super P:PVDF)	1 M $LiPF_6$ in EC/DEC/EMC = 1:1:1 (v/v)	3.5-5.0	120, 1 C	98.99 % after 200 cycles	26
PVDF, Sucrose	75:15:10 (AM:Super P:PVDF)	1 M $LiPF_6$ in EC/DMC = 1:1 (v/v)	3.5-5.0	129.7, C/2	68 % after 100 cycles	27
Sucrose	70:20:10 (AM:AB:PVDF)	1 M LiPF6 in EC/PC/DMC = 1:1:1 (v/v) with 2 wt.% TMSP	3.5-5.0	163, 1 C	76.36 % after 100 cycles	Our work

AM: Active materials; CB: Carbon black; PVDF: Polyvinylidene difluoride; EC: Ethylene carbonate; DMC: Dimethyl carbonate; AB: Acetylene black; DEC: Diethyl carbonate; EMC: Ethyl methyl carbonate; FEC: Fluoroethylene carbonate; PEDOT: Poly(3,4-ethylenedioxythiophene; MWCNT: Multi-walled carbon nanotubes, PVP: Polyvinylpyrrolidone; PTFE: Polytetrafluoroethylene; CMC: Carboxy methyl cellulose; CTAB: Cetyltrimethylammonium bromide; TPN: Thiophene; TMSP: Tris(trimethylsilyl) phosphite

Table S4. Summary of Coulombic efficiency statistics and standard deviations of ST-A-LCP electrodes at different C-rates.

C-rates	Minimum	Maximum	Range	Mean value
C/10	58.89	92.74	33.85	85.12
C/5	65.72	93.37	27.65	91.53
C/2	69.79	97.96	28.17	97.05
1 C	75.22	99.31	24.09	98.57

Table S5. Summary of Coulombic efficiency statistics and standard deviations of ST-C-LCP electrodes at different C-rates.

C-rates	Minimum	Maximum	Range	Mean value
C/10	55.54	91.36	35.81	79.90
C/5	66.25	94.64	28.39	91.58
C/2	71.79	97.33	25.54	96.52
1 C	78.25	99.82	21.57	99.10

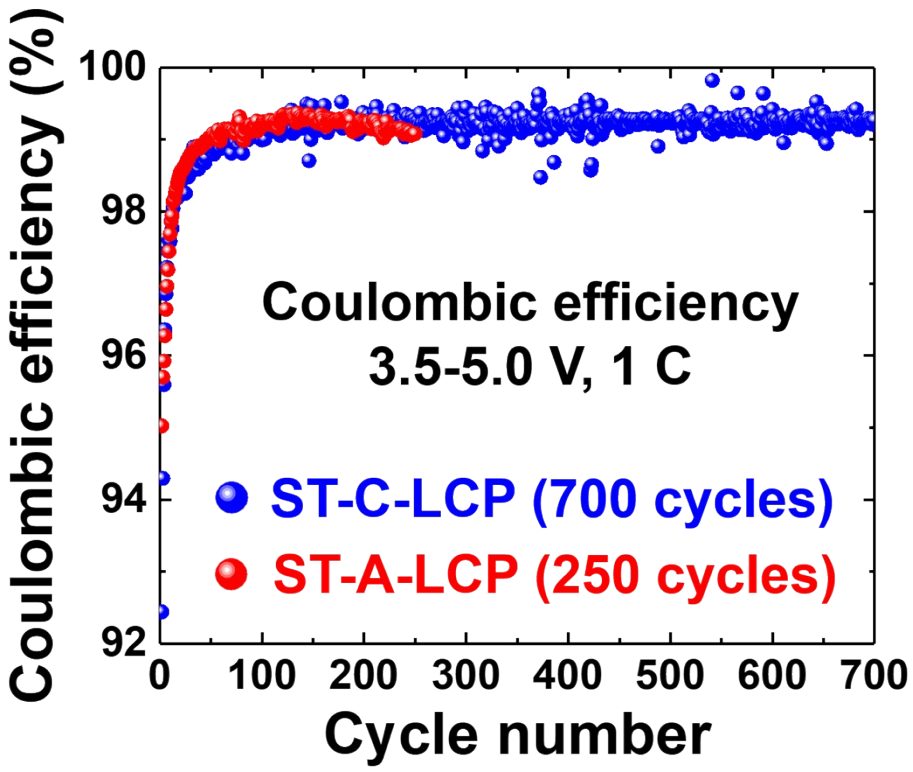

Figure S9. Coulombic efficiency comparison of ST-A-LCP and ST-C-LCP.

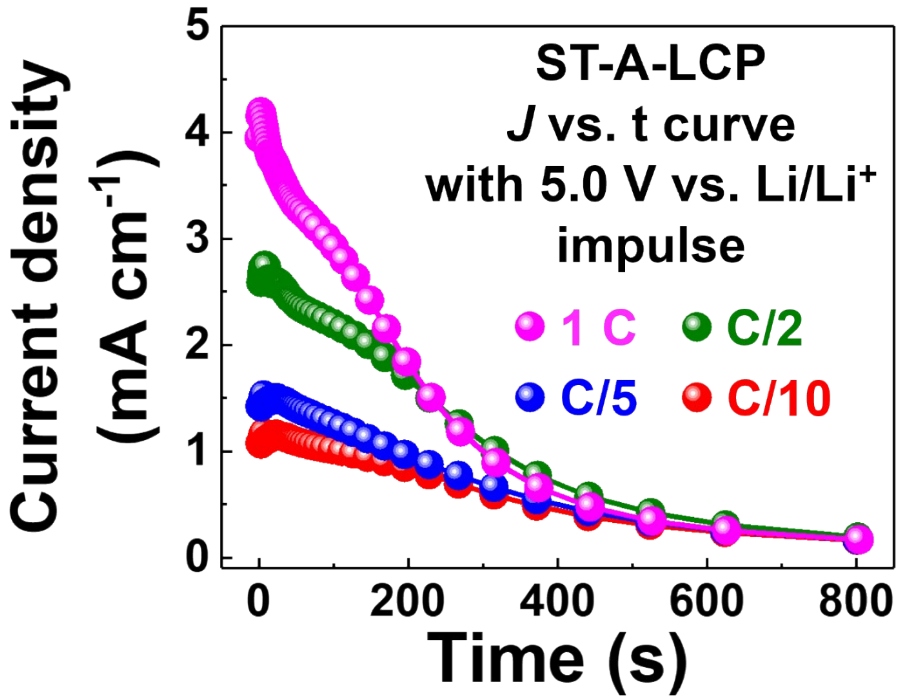

Figure S10. Current density vs. time (*J*-*t*) of cycled ST-A-LCP electrodes at different C-rates after 10 cycles, measured from the Nyquist plot with 5.0 V vs. Li/Li^+ impulse.

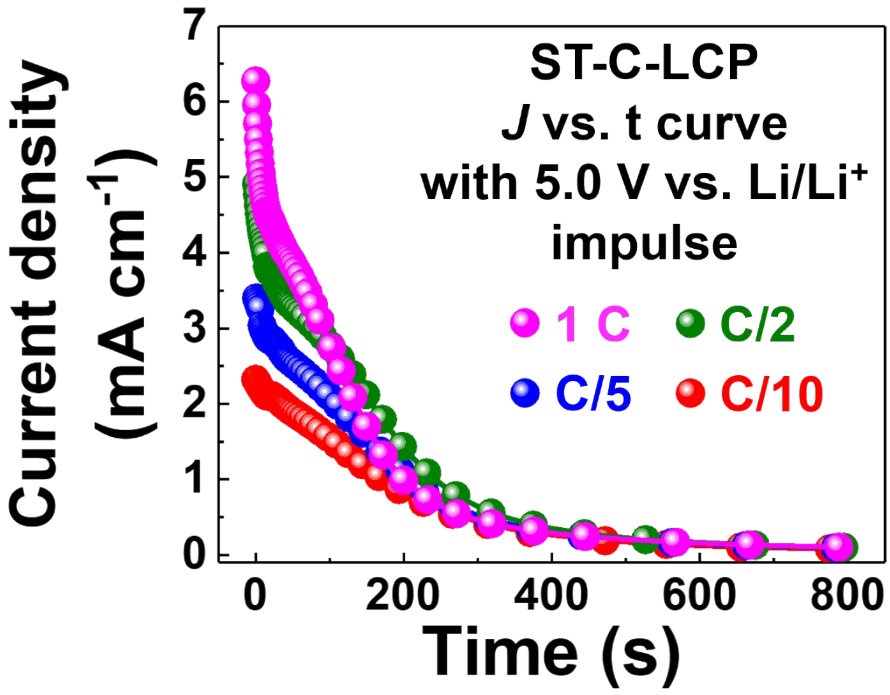

Figure S11. Current density vs. time (*J*-*t*) of cycled ST-C-LCP electrodes at different C-rates after 10 cycles, measured from the Nyquist plot with 5.0 V vs. Li/Li^+ impulse.

Table S6. XPS peak data summary of pristine ST-A-LCP electrodes.

Peak	Bond	Binding energy (eV)	FWHM (eV)	Atomic %
C 1s	C-C & C-H	284.75	0.81	54.5
	C-O	285.70	1.24	14.34
	C-F	286.69	1.36	13.00
	C=O	287.73	1.34	2.86
	O-C=O	288.98	1.39	2.76
	CH_2-CF_2	291.09	1.72	12.54
O 1s	C=O & O-C=O	531.85	1.89	96.05
	C-O	533.69	1.16	3.95
F 1s	Li-F & Co-F	685.37	0.86	0.65
	C-F	687.93	1.81	97.11
	CH_2-CF_2	690.21	2.43	2.24

Table S7. XPS peak data summary of pristine ST-C-LCP electrodes**.**

Peak	Bond	Binding energy (eV)	FWHM (eV)	Atomic %
C 1s	C-C & C-H	284.81	0.87	62.89
	C-O	285.72	0.75	7.60
	C-F	286.40	0.97	7.66
	C=O	287.06	1.33	6.66
	O-C=O	288.78	2.49	5.40
	CH_2-CF_2	291.13	1.63	9.79
O 1s	C=O & O-C=O	531.86	1.45	78.74
	C-O	533.25	1.88	21.26
F 1s	Li-F & Co-F	685.84	0.52	0.48
	C-F	687.98	1.78	97.70
	CH_2-CF_2	689.73	1.90	1.82

Table S8. XPS peak data summary of ST-A-LCP electrodes after 250 cycles at 1 C.

Peak	Bond	Binding energy (eV)	FWHM (eV)	Atomic %
C 1s	C-C & C-H	284.75	1.07	39.62
	C-O	285.88	1.09	17.19
	C-F	286.78	1.38	20.15
	C=O	288.13	1.19	4.18
	O-C=O	289.23	1.14	2.95
	CH_2-CF_2	290.67	1.29	15.90
O 1s	C=O & O-C=O	531.78	1.64	57.97
	C-O	533.35	1.93	42.03
F 1s	Li-F & Co-F	686.38	3.2	3.82
	C-F	688.00	1.89	96.18
	CH_2-CF_2	690.90	0.62	0

Table S9. XPS peak data summary of ST-C-LCP electrodes after 700 cycles at 1 C.

Peak	Bond	Binding energy (eV)	FWHM (eV)	Atomic %
C 1s	C-C & C-H	284.75	0.94	35.94
	C-O	285.93	1.27	17.20
	C-F	286.76	1.21	18.26
	C=O	287.71	1.11	3.68
	O-C=O	289.11	2.09	5.85
	CH_2-CF_2	290.96	1.27	19.07
O 1s	C=O & O-C=O	531.91	1.71	57.92
	C-O	533.59	1.99	42.08
F 1s	Li-F & Co-F	685.95	1.6	18.94
	C-F	688.00	1.84	80.94
	CH_2-CF_2	690.58	0.51	0.12

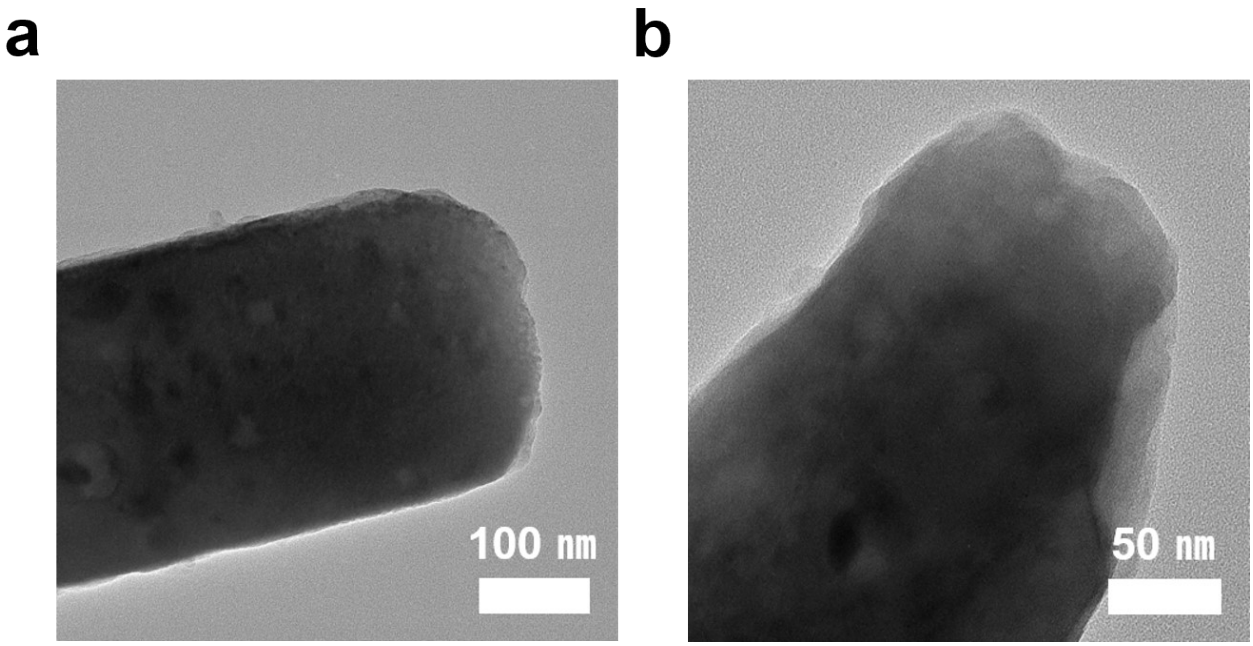

Figure S12. HRTEM images of (a) ST-C-LCP and (b) ST-A-LCP samples after 100 cycles at 1 C.

Table S10. XPS peak data summary of collected separator from the cycled cells with ST-A-LCP cathode after 100 cycles at 1 C.

Peak	Bond	Binding energy (eV)	FWHM (eV)	Atomic %
Co 2p $_{3/2}$	Co^{3+}	780.94	2.27	14.84
	Co^{2+}	782.39	3.37	27.16
	Co^{3+} Sat.	785.71	3.37	16.06
	Co^{2+} Sat.	788.76	3.37	8.88
Co 2p $_{1/2}$	Co^{3+}	796.95	2.33	5.73
	Co^{2+}	797.77	2.56	10.39
	Co^{3+} Sat.	800.71	3.37	8.58
	Co^{2+} Sat.	804.06	3.37	8.36

***Sat.: Satellite**

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