Supporting Information

Optimized Functional Additive Enabled Stable Cathode and Anode Interfaces for High-voltage All-Solid-State Lithium Batteries with Significantly Improved Cycling Performance

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Keywords: Functional additive, Interface stability, High-voltage, All-solid-state battery, Lithium metal battery

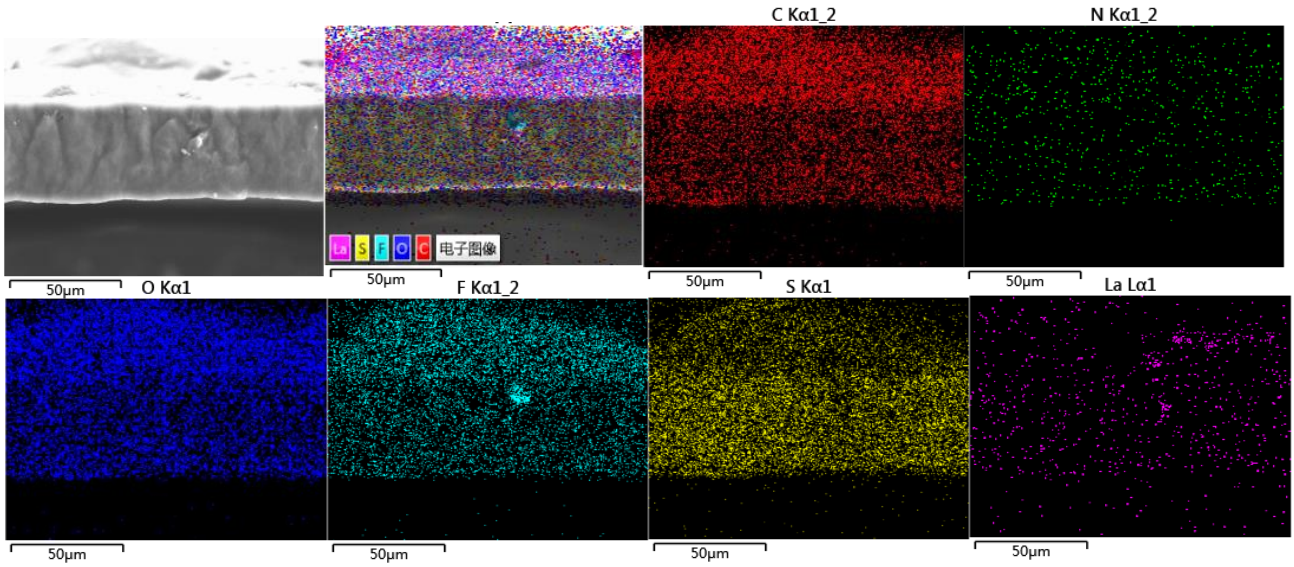

Fig. S1. The EDS mappings of the cross-section of the as-prepared additive-free CSE film.

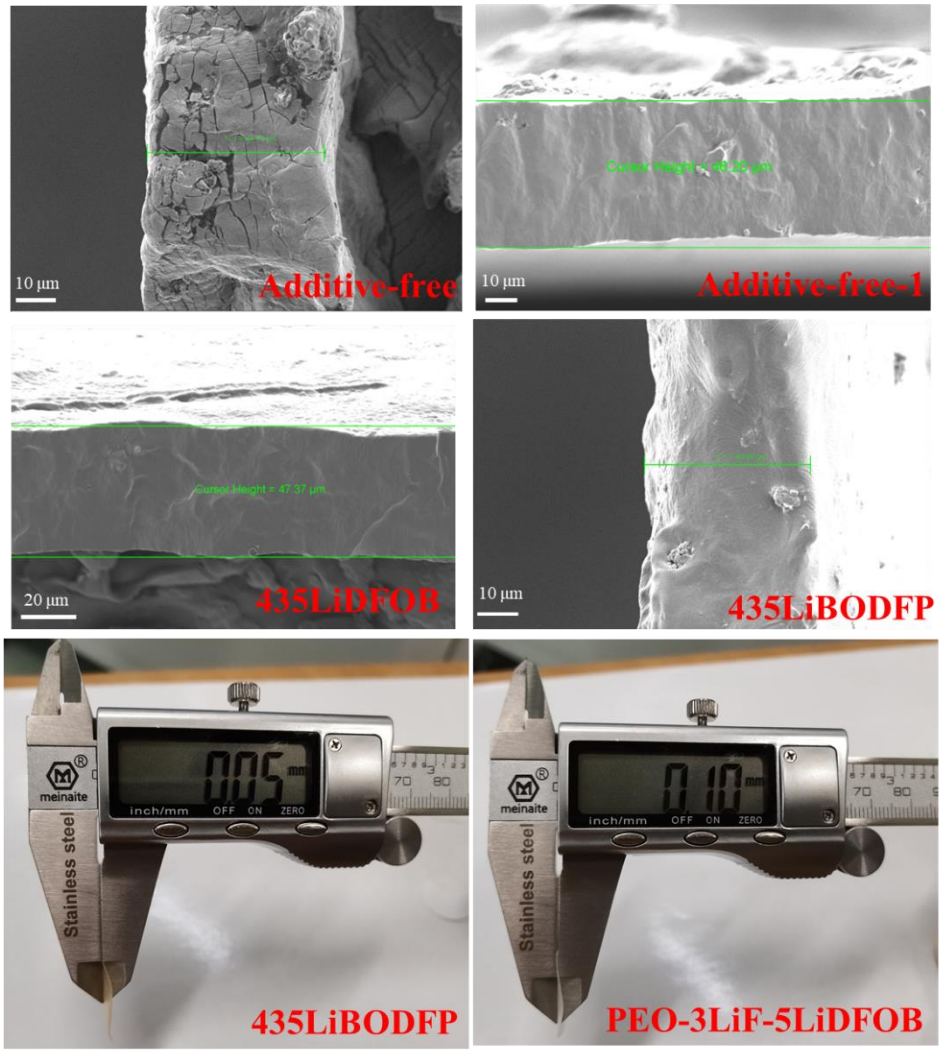

Fig. S2. The thicknesses of the as-prepared CSEs.

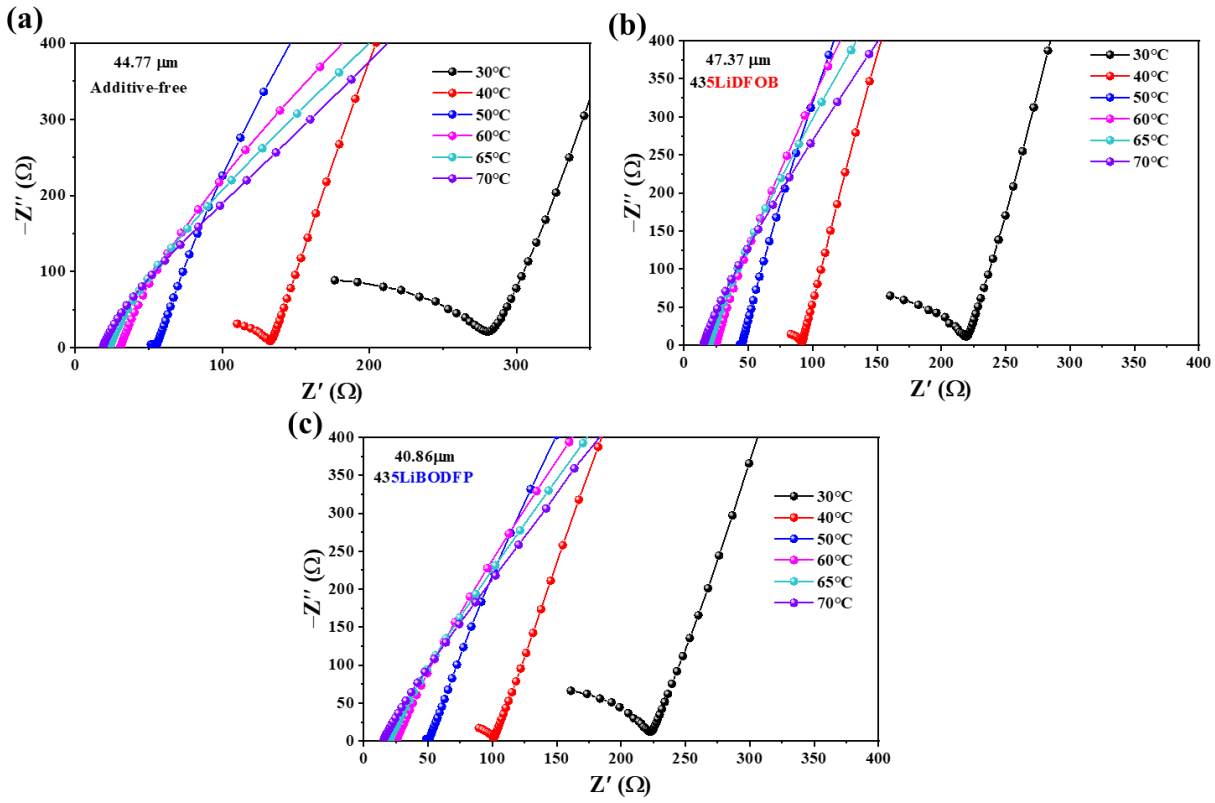

Fig. S3. Nyquist plots of (a) additive-free, (b) 435LiDFOB and (c) 435LiBODFP CSEs at different temperatures.

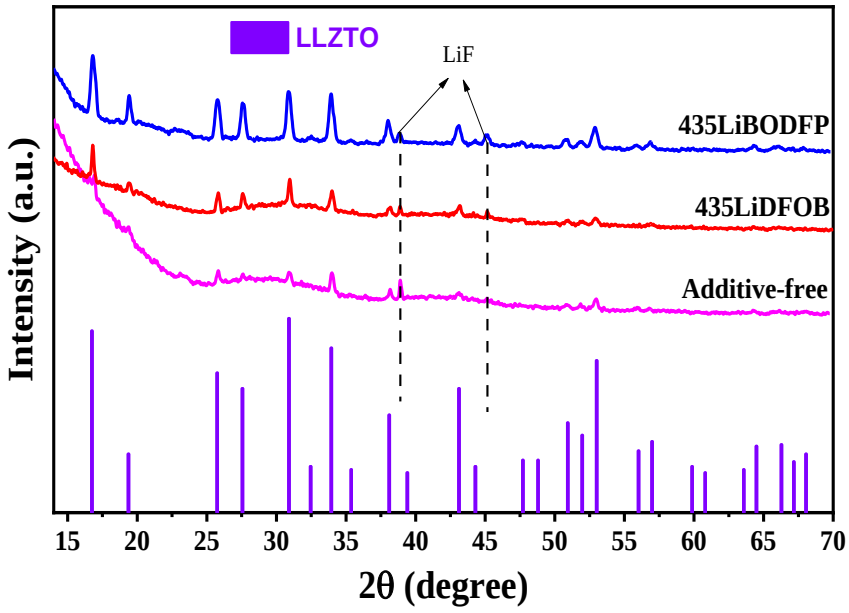

Fig. S4. XRD patterns of the as-prepared CSEs with different additives.

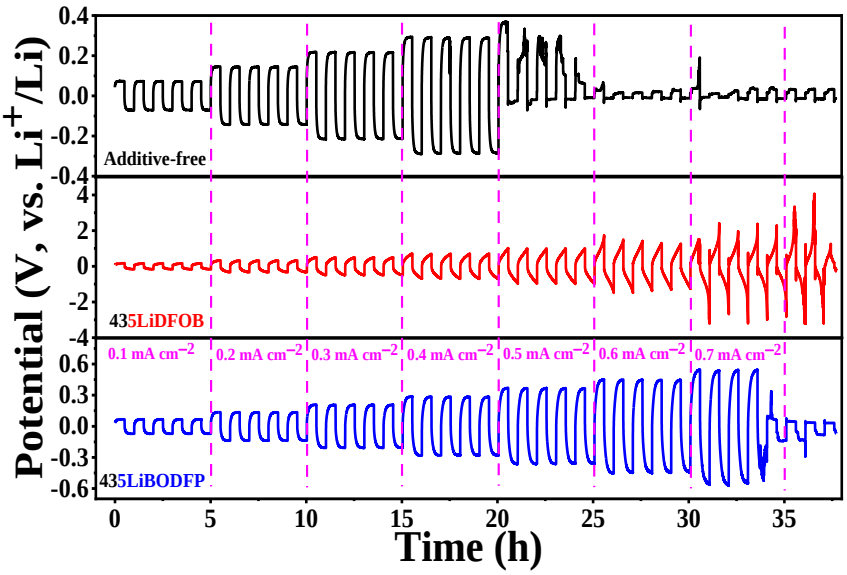

Fig. S5. The critical current densities of the Li/Li symmetrical batteries assembled by CSEs with different additives.

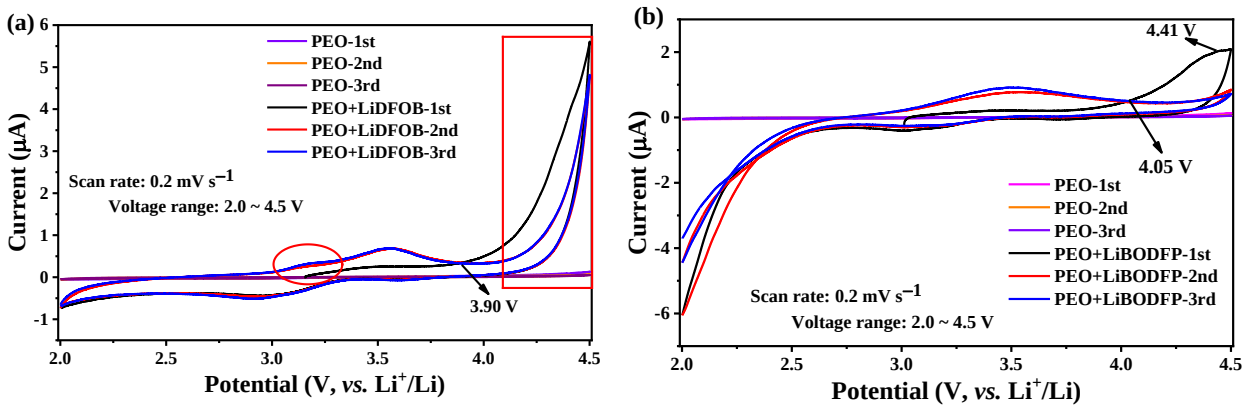

Fig. S6. CV results of (a) PEO+LiDFOB and (b) PEO+LiBODFP at a scan rate of 0.2 mV s^{-1} in the voltage range of 2.0 ~ 4.5 V.

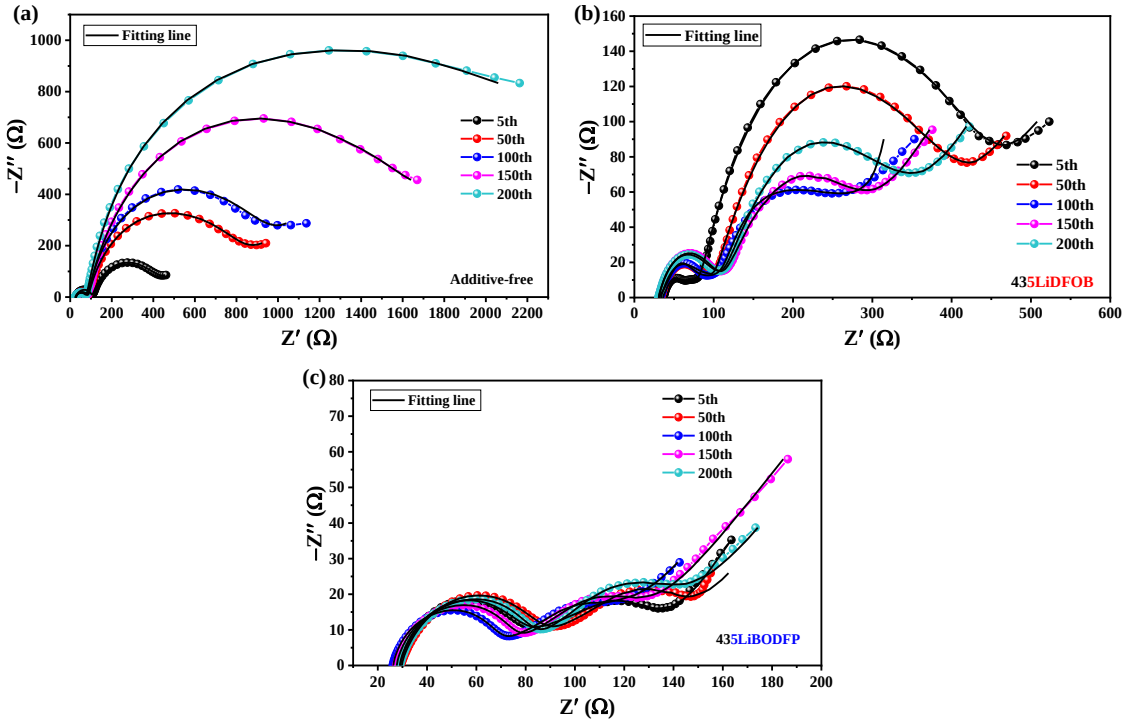

Fig. S7. The fitting results of the acquired EIS curves for cells assembled by (a) additive-free, (b) 435LiDFOB and 435LiBODFP CSEs after different cycles.

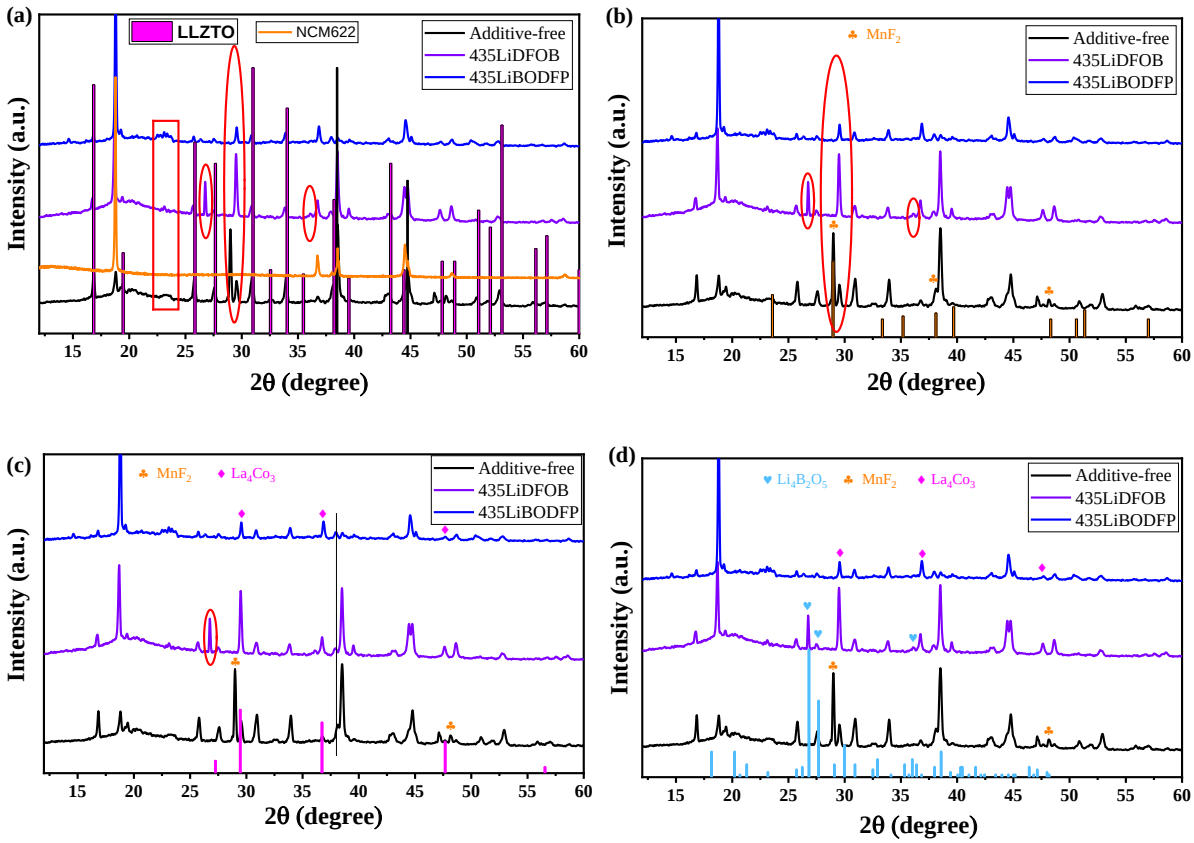

Fig. S8. XRD results of the cycled cathodes paired with CSEs consisting of different additives; (a) new appeared peaks marked with red lines, (b) peaks matched with MnF_2 (PDF#17-0864), (c) peaks matched with La_4Co_3 (PDF#21-0262), (d) peaks matched with $Li_4B_2O_5$ (PDF#18-0719).

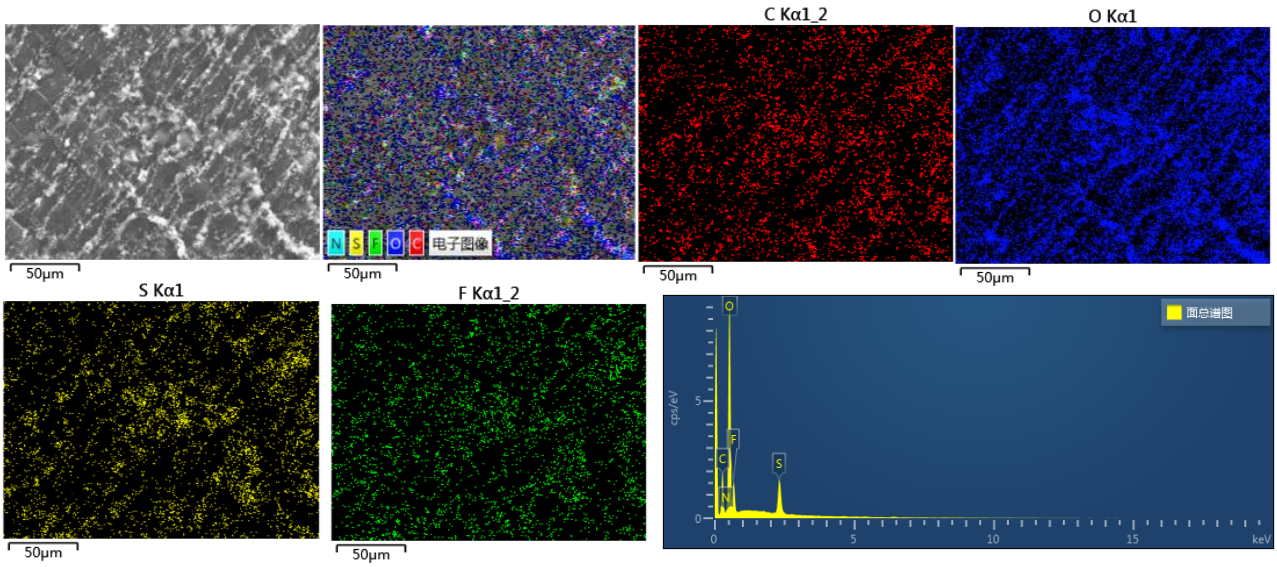

Fig. S9. EDX results of the surface of the cycled Li anode paired with additive-free CSE.

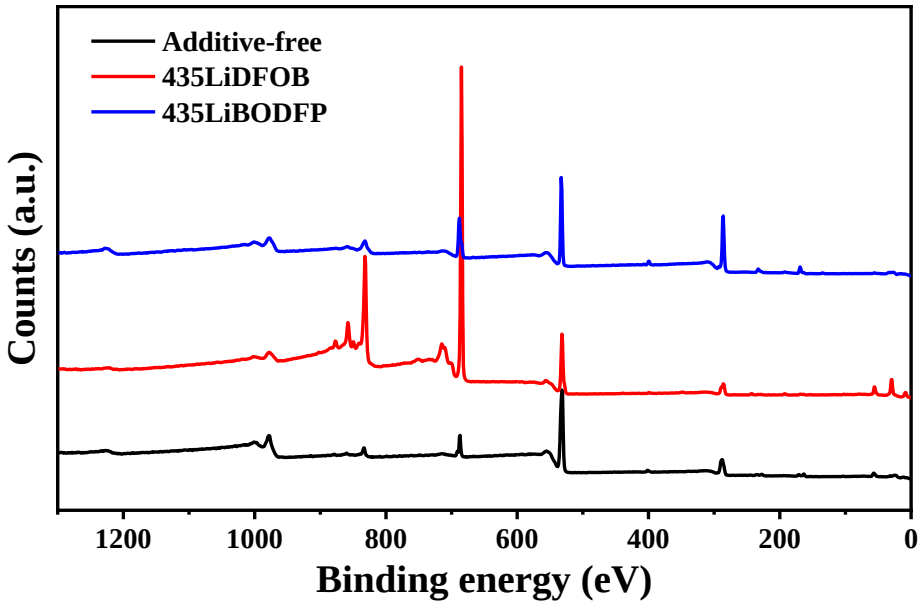

Fig. S10. XPS scan results of the cycled Li anodes paired with CSEs with different additives.

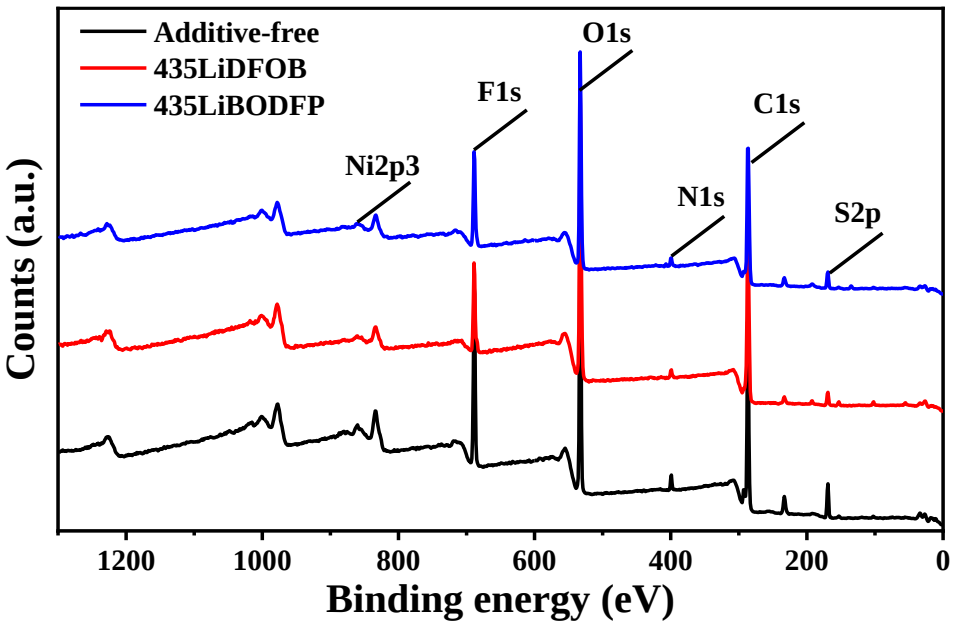

Fig. S11. XPS scan results of the cycled cathodes paired with CSEs with different additives.

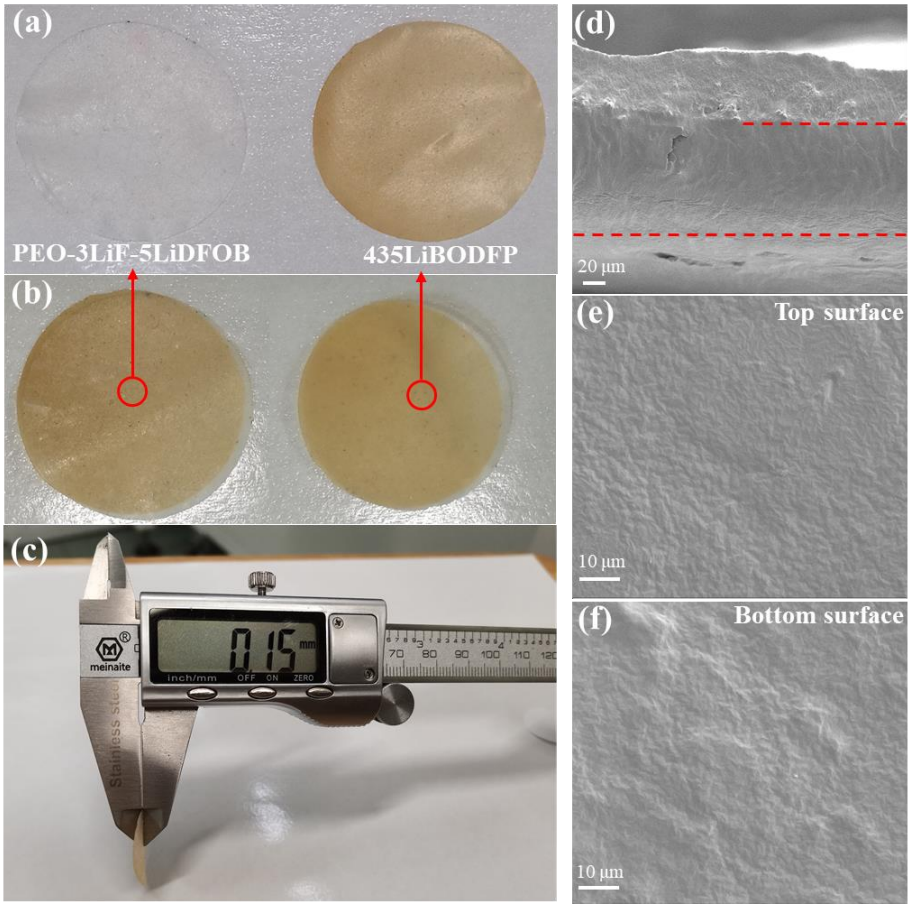

Fig.S12. (a-b) Photographs of the as-prepared CSEs, (b) the thickness of the double-layer CSE, and SEM images of the prepared double-layer CSE: (d) the cross-section, (e) top surface and (f) bottom surface.

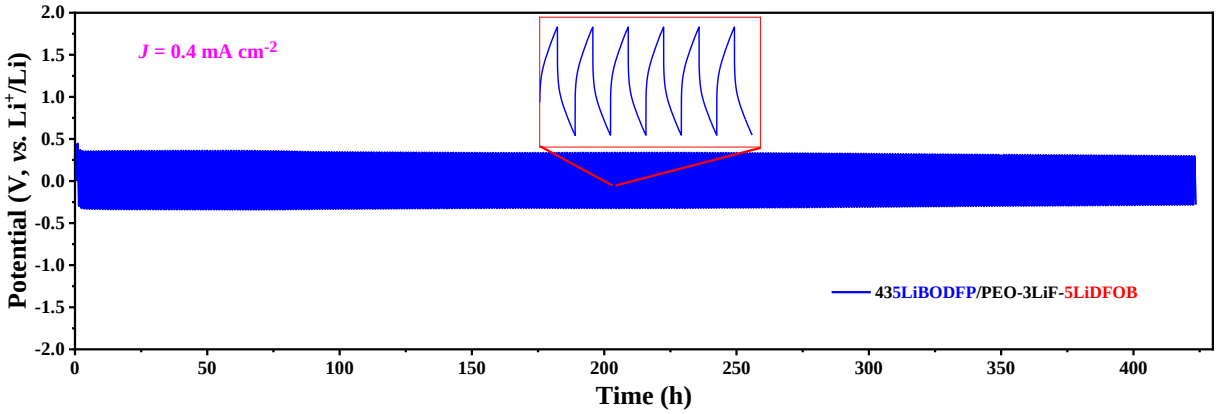

Fig. S13. The cycle stability of Li/Li symmetrical cell assembled by 435LiBODFP/PEO-3LiF-5LiDFOB double-layer CSE.

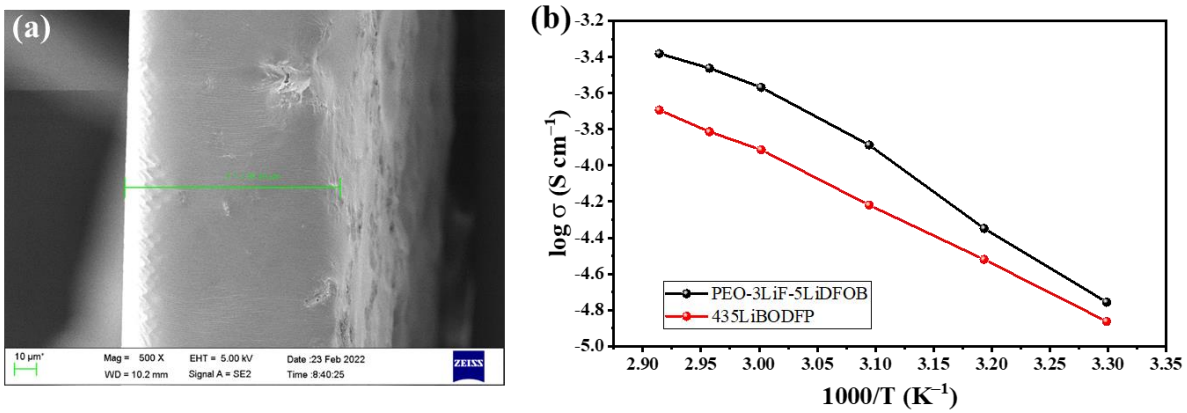

Fig. S14. (a) The thickness of the as-prepared PEO-3LiF-5LiBODFP CSE, (b) ionic conductivities of 435LiBODFP and PEO-3LiF-5LiBODFP CSEs at different temperatures.

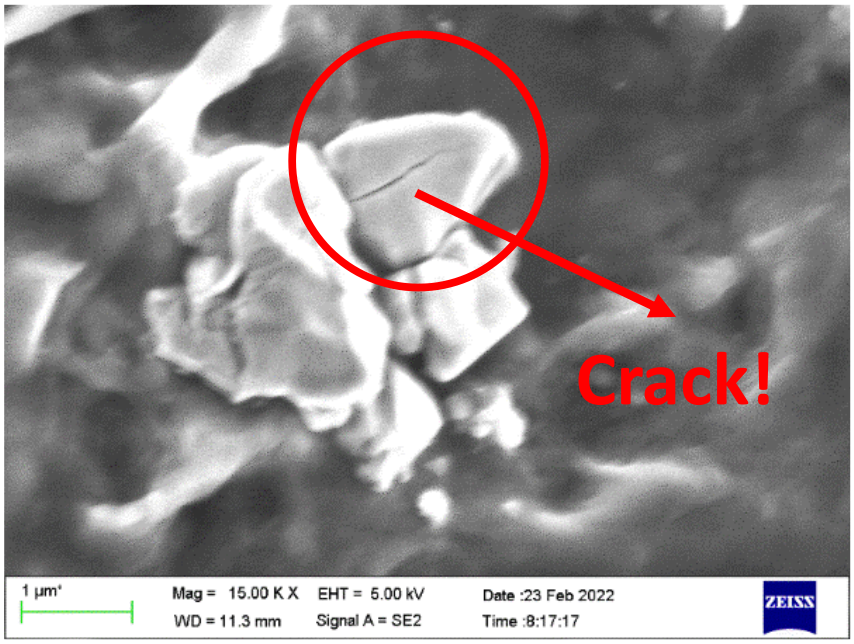

Fig. S15. SEM image of the cycled cathode active material.

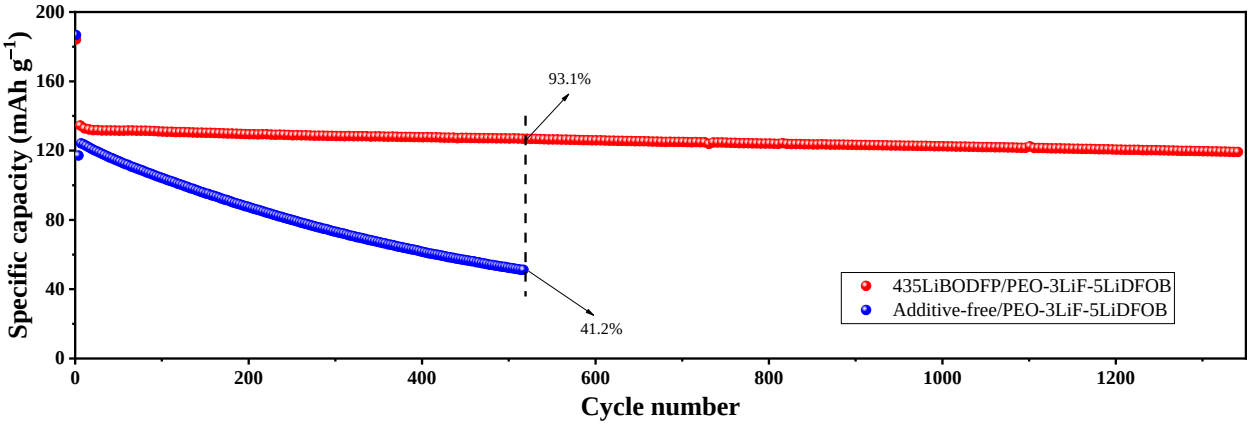

Fig. S16. The cycle stability of cells assembled by double-layer CSEs at 1.0 C

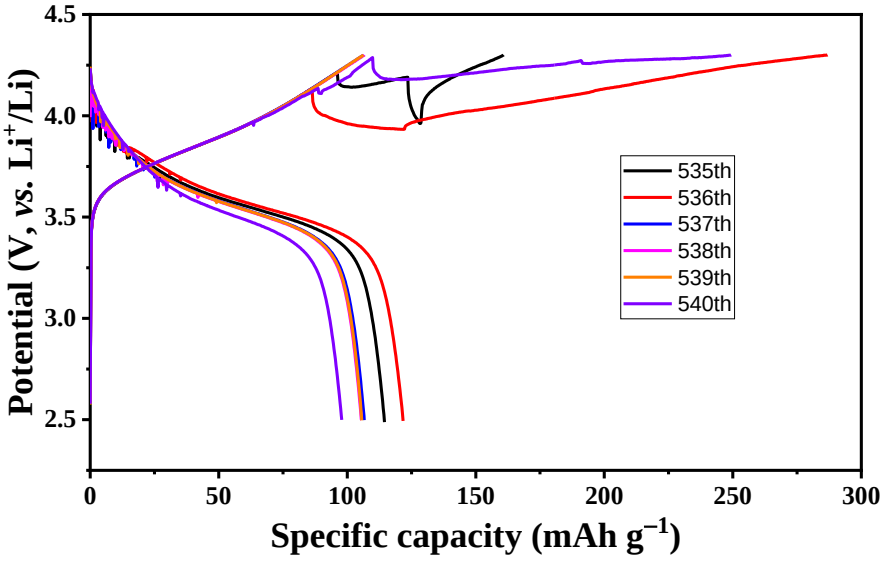

Fig. S17. The charge-discharge curves of SC622/435LiBODFP/Li cell at cycles of 535th ~ 540th.

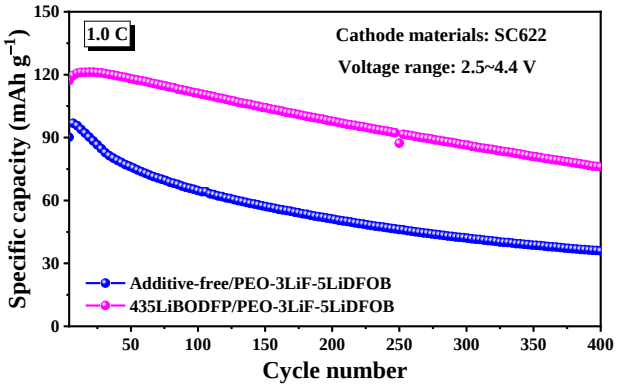

Fig. S18. Cycle performance of the assembled cells with double-layer CSE at 1.0 C and in the voltage range of 2.5~4.4 V.

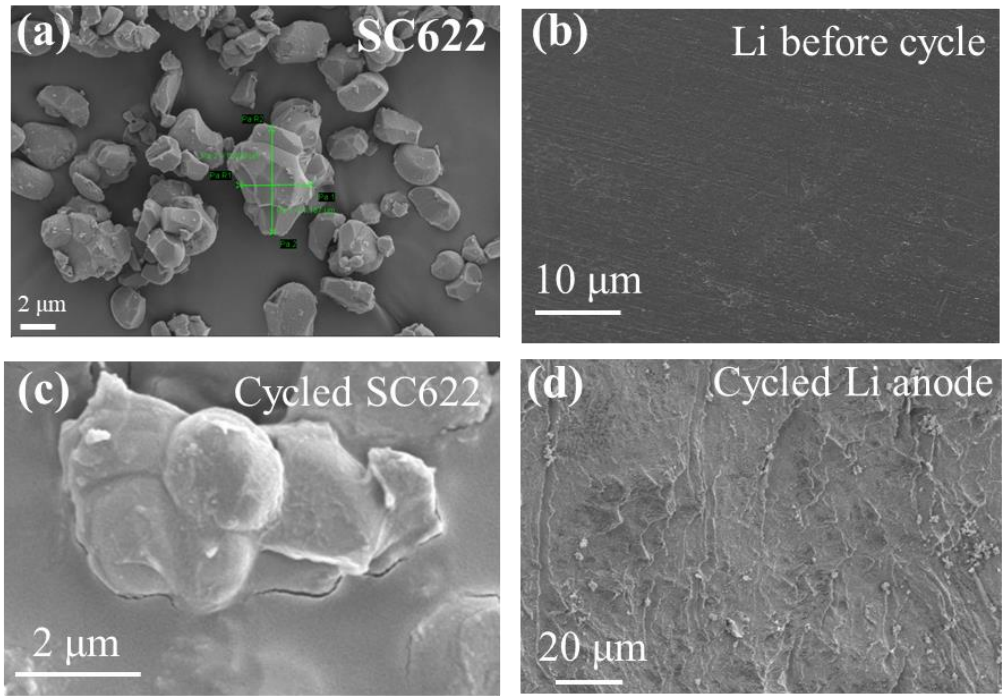

Fig. S19. The SEM images of (a) SC622 materials and (b) uncycled Li metal; the SEM images of the cycled electrodes disassembled from cell after 1340 cycles: (c) cycled SC622 cathode and (d) cycled Li anode.

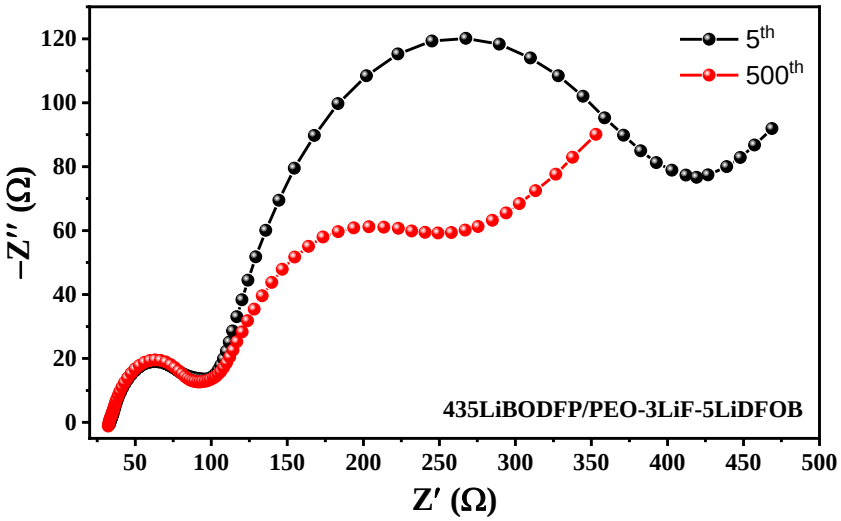

Fig. S20. EIS results of cell assembled by 435LiBODFP/PEO-3LiF-5LiDFOB double-layer CSE after different cycles.

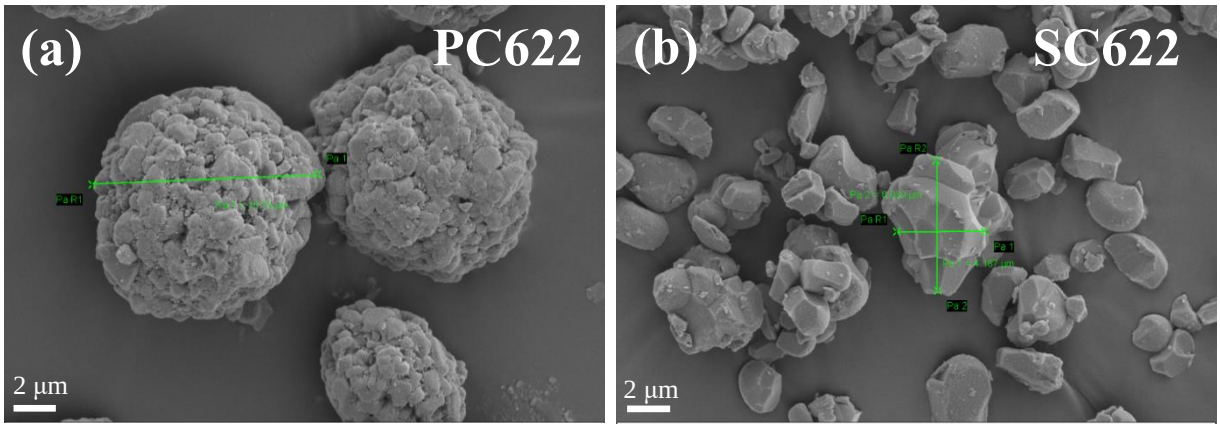

Fig. S21. SEM images of the used cathode active materials: (a) polycrystalline $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (PC622) and (b) single crystal $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ (SC622).

Table S1 The fitting results of the cells assembled by CSEs with different additives after different cycles.

Sample	Cycle number	SE (Ω)	Cathode interface (Ω)	Anode interface (Ω)	Total (Ω)
Additive-free	5th	28.11	300.10	77.80	406.01
	50th	26.15	682.20	59.47	767.82
	100th	26.35	782.2	54.07	862.62
	150th	27.06	1611	58.84	1696.90
	200th	24.27	1993	59.35	2076.62
435LiBODFP	5th	28.44	57.78	50.37	136.59
	50th	29.09	58.74	60.56	148.39
	100th	25.85	52.89	45.7	124.44
	150th	27.08	49.67	50.41	127.16
	200th	28.54	53.50	57.20	139.24
435LiDFOB	5th	35.13	347.9	47.15	430.18
	50th	33.62	295.2	65.40	394.22
	100th	32.5	185.2	60.9	278.6
	150th	29.66	199.7	78.65	308.01
	200th	30.24	231.6	77.96	339.8