Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Engineering the Conductive Carbon/PEO Interface to Stabilize Solid Polymer Electrolytes for All-Solid-State High Voltage $LiCoO_2$ Batteries

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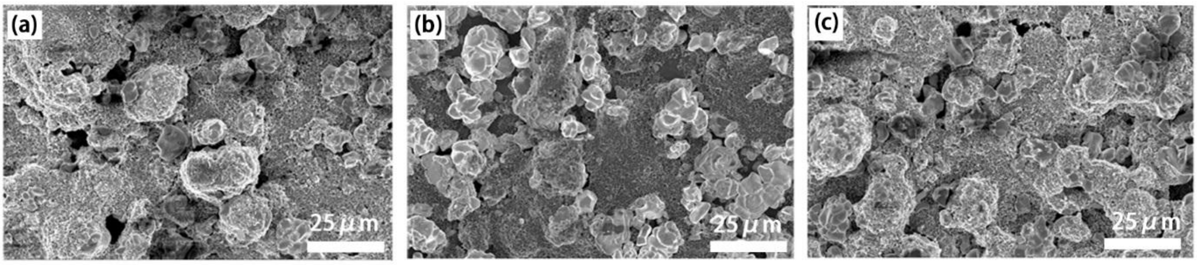

Fig. S1 SEM images of (a) bare LCO electrode, (b) electrode with ALD LTO coated $LiCoO_2$ particles (LCO-coating protection) and (c) ALD LTO coated electrode (LCO+CB-coating protection).

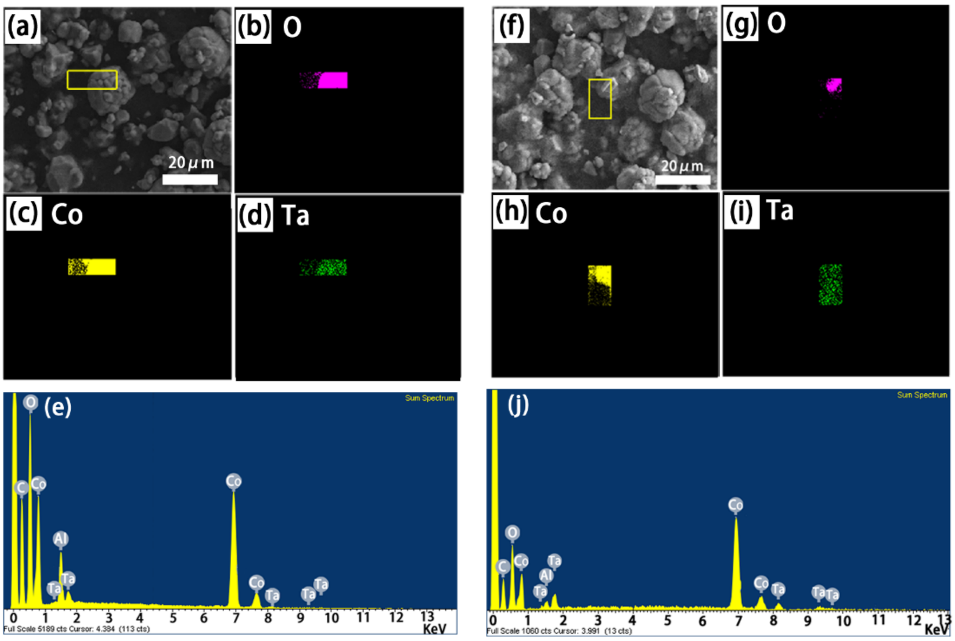

Fig. S2 (a) SEM image and EDX mappings of selected area for electrode with 50 cycles ALD LTO coated $LiCoO_2$ particles (LCO-coating protection) and its corresponding (b)

O mapping, (c) Co mapping, (d) Ta mapping and the corresponding EDX spectrum (e). (f) SEM image and EDX mappings of selected area for 50 cycles ALD LTO coated electrode (LCO+CB-coating protection) and its corresponding (g) O mapping, (h) Co mapping, (i) Ta mapping and the corresponding EDX spectrum (j).

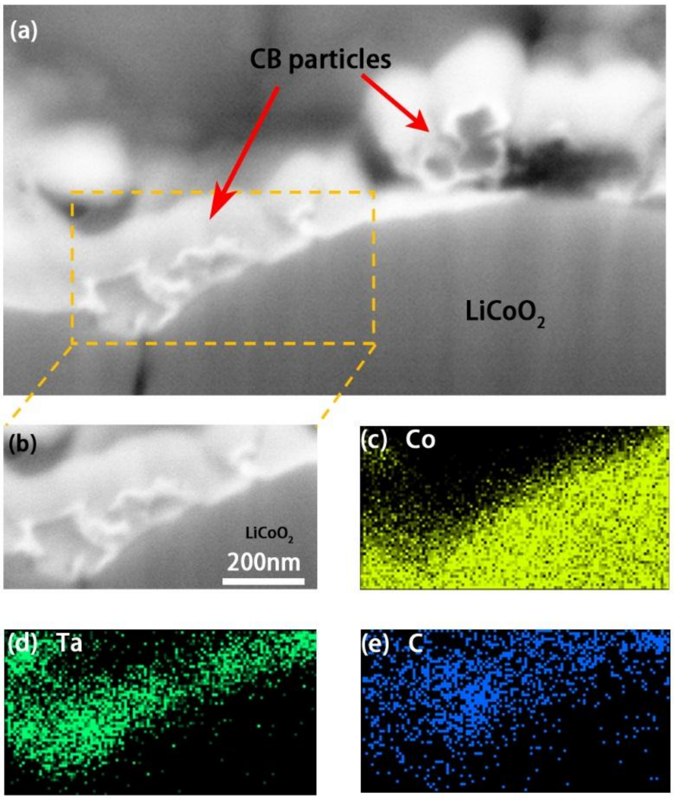

Fig. S3 (a) Cross-section view of SEM image of LiCoO$_2$ particle covered with carbon black particles with LTO coating. (b) The selected area for EDX mapping and its corresponding element distribution of (c) Co, (d) Ta, (e) C.

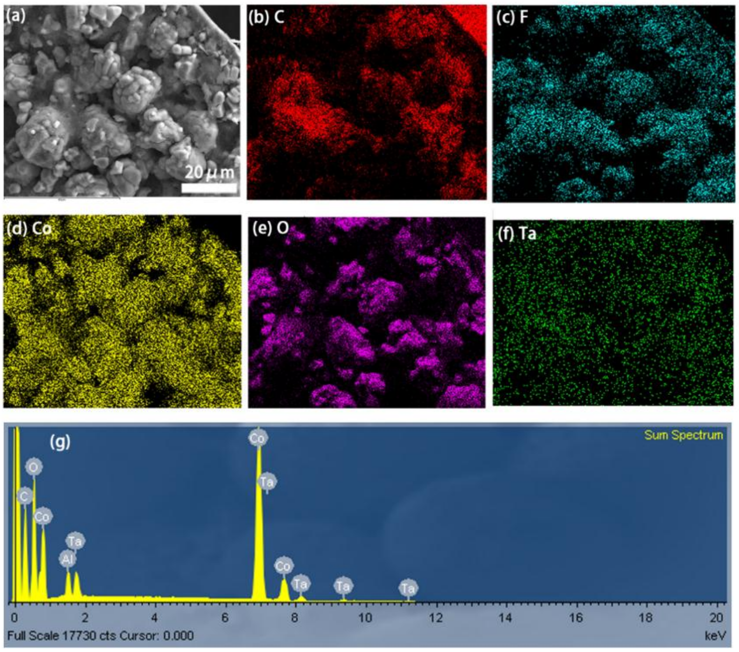

Fig. S4 SEM image and EDX mappings of ALD LTO coated $LiCoO_2$ electrode. (a) SEM image; EDX mappings of (b) C, (c) F, (d) Co, (e) O, and (f) Ta elements. (g) Corresponding EDX spectrum.

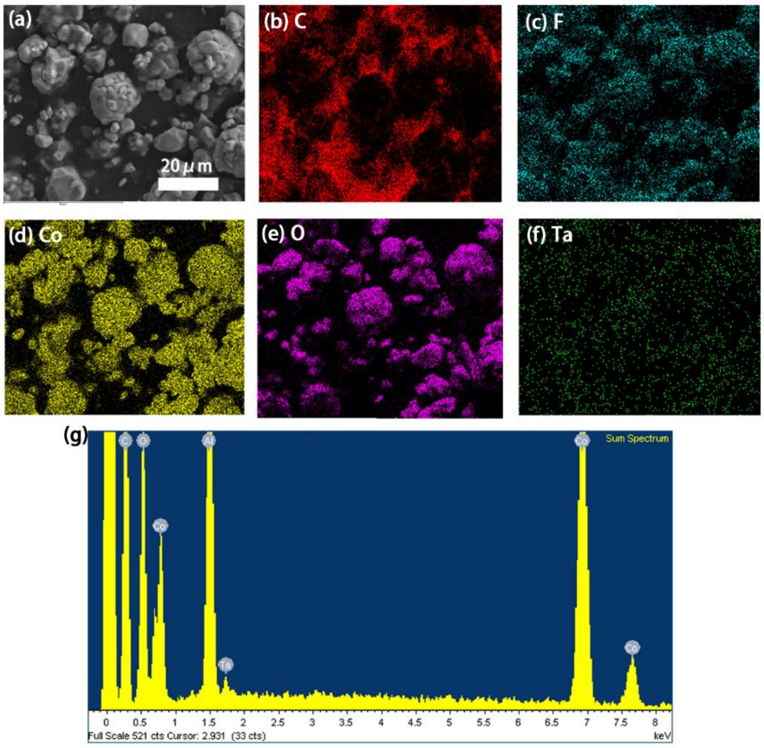

Fig. S5 SEM image and EDX mappings of the electrode with ALD LTO coated $LiCoO_2$ particles. (a) SEM image; EDX mappings of (b) C, (c) F, (d) Co, (e) O, and (f) Ta elements. (g) Corresponding EDX spectrum.

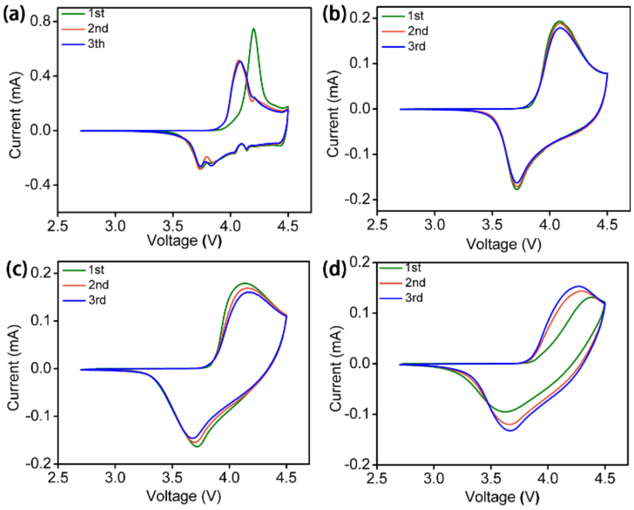

Fig. S6 CV of (a) liquid electrolyte-based $LiCoO_2$ battery, ASSLBs with (b) bare $LiCoO_2$, (c) $LiCoO_2$ particles coating and (d) $LiCoO_2$ electrode coating. All batteries were tested at 60°C.

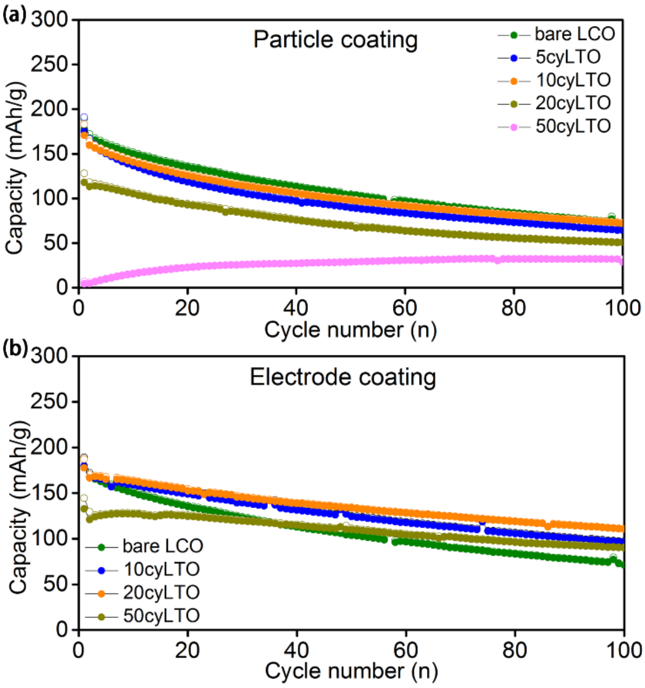

Fig. S7 The influences of ALD coating thickness on the performances of ASSLBs with (a) particles coating and (b) electrode coating.

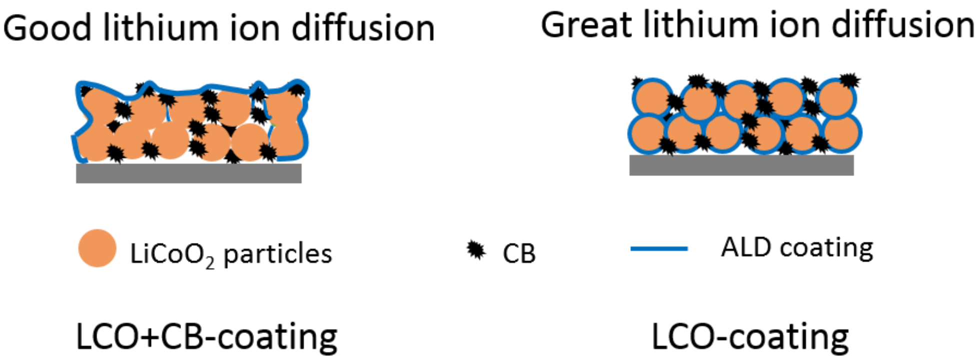

Fig. S8 Comparison of ALD coating in LCO+CB-coating electrode and LCO-coating electrode. A better lithium ion diffusion can be achieved in LCO-coating electrode.

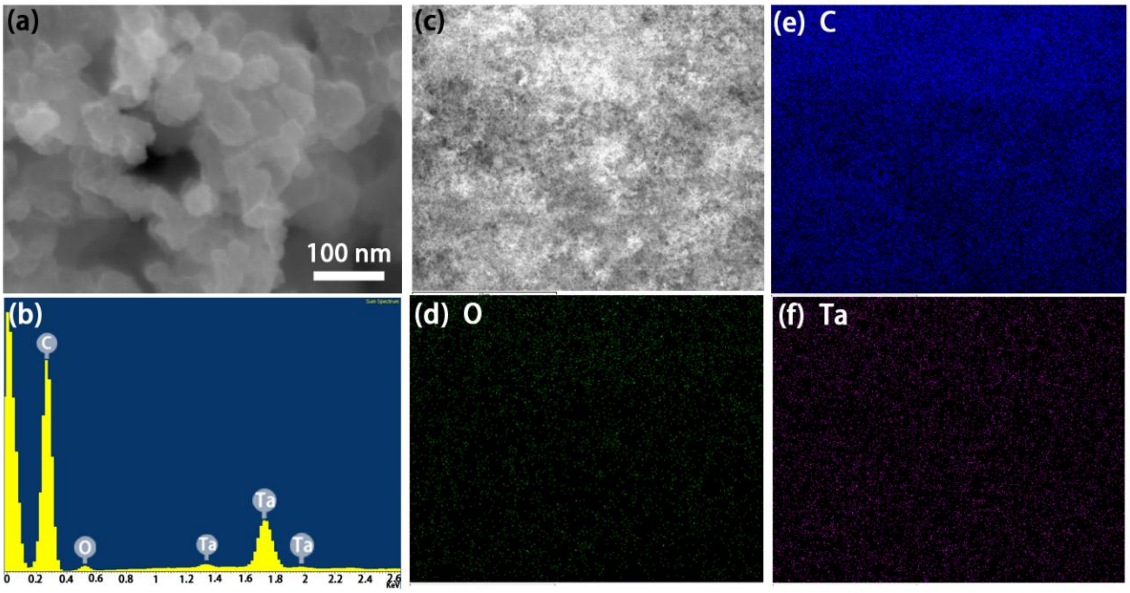

Fig. S9 (a) SEM image of carbon black particles with ALD-LTO coating. (b) EXD spectrum of carbon black particles with ALD-LTO coating; (c) corresponding SEM image of EDX mapping area; (d) corresponding O distribution; (c) corresponding C distribution; (d) corresponding Ta distribution.

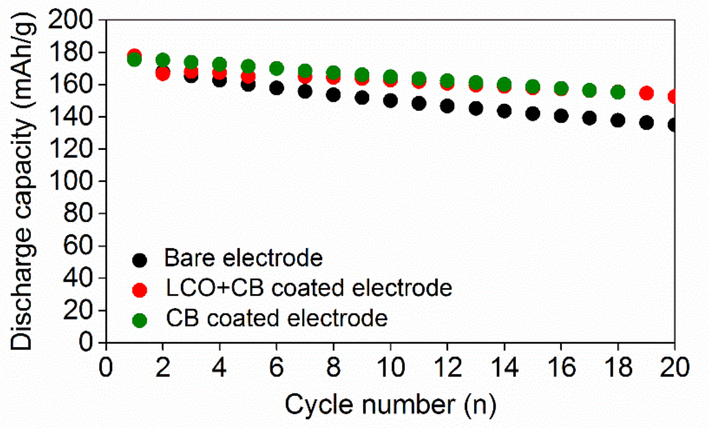

Fig. S10 Comparison of cycling performance of the ASSLBs with bare $LiCoO_2$ electrode, LCO+CB coated electrode and CB coated $LiCoO_2$ electrode.

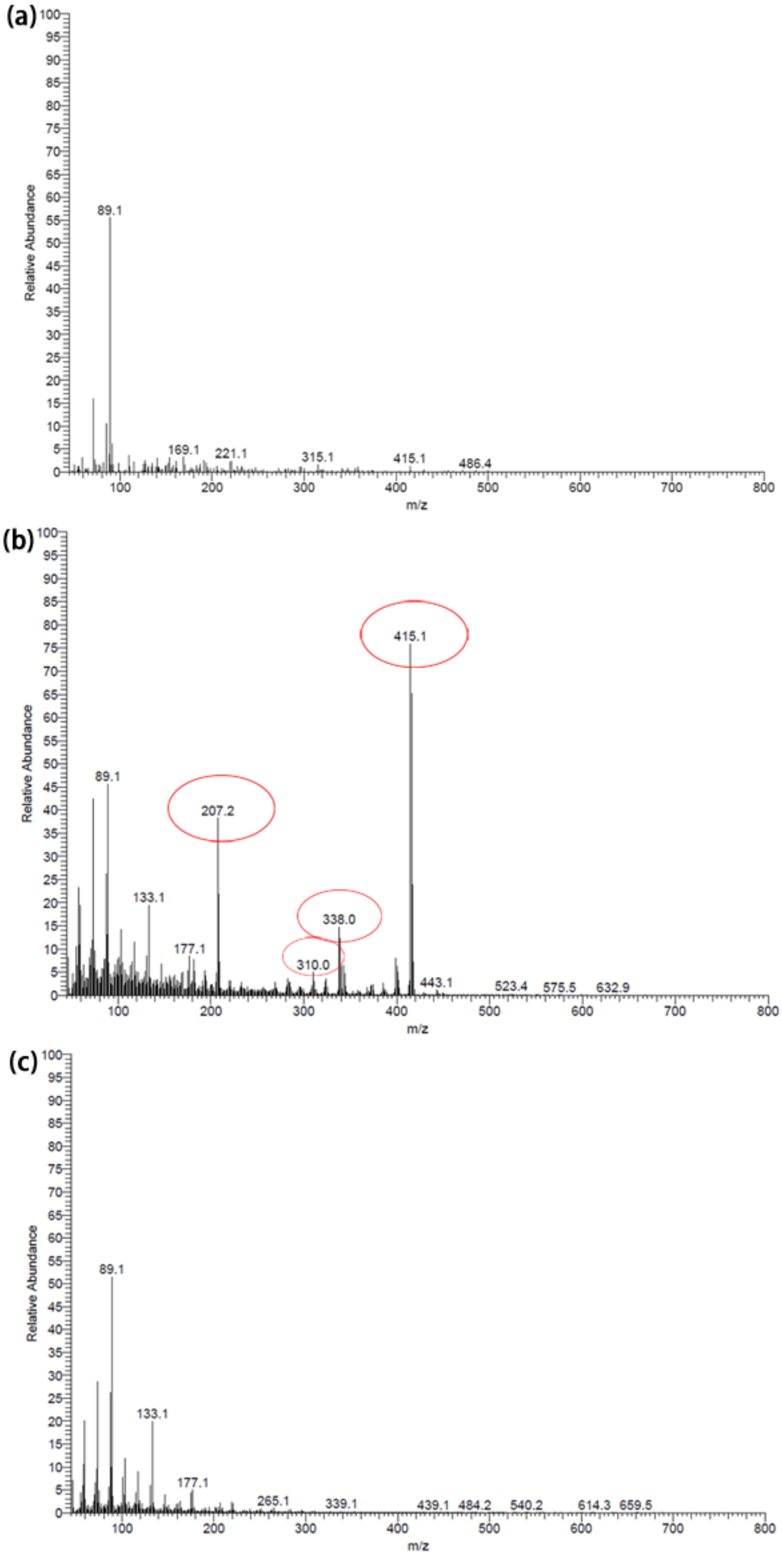

Fig. S11 The mass spectrometry (MS) results. (a) Pristine PEO-based SPE. (b) PEO-carbon composite after charging to 4.5 V and holding for 20 h; the red circles point out the signals related to the decomposition of PEO-based SPE. (c) PEO-ALD LTO carbon composite after charging to 4.5 V and holding for 20 h. Compared with the plot of pristine PEO-based SPE, the additional peaks marked by red circle and the increased intensities of light MS peaks suggested the partial depolymerization of PEO under high voltage, while this phenomenon is not so clear for PEO-ALD LTO carbon composite, suggesting that the decomposition of PEO can be restricted.

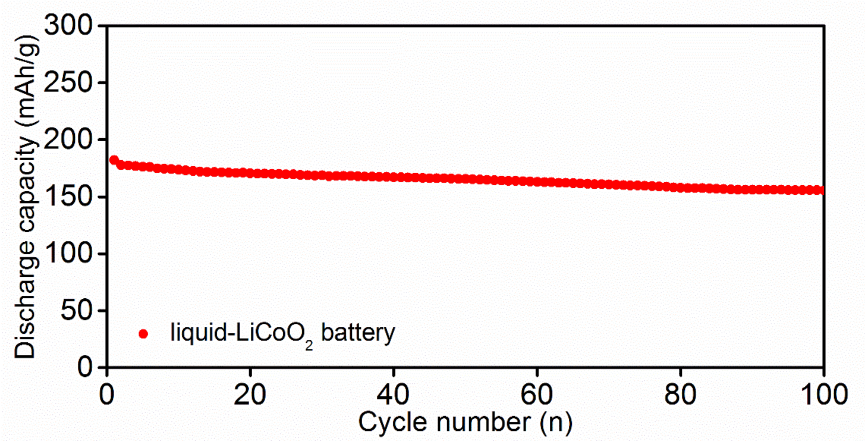

Fig. S12 Cycling performance of $LiCoO_2$ battery with carbonate-based liquid electrolyte. The charge/discharge voltage window is from 2.7 – 4.5 V. The stable performance indicates the $LiCoO_2$ particles are stable. The protection may not be so critical for performance enhancement. Thus, the capacity decay of the $LiCoO_2$ ASSB is the contribution of the decomposition of SPE.

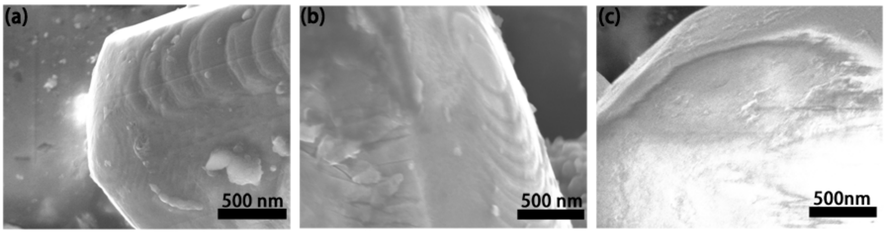

Fig. S13 SEM images of $LiCoO_2$ particles collected from ASSLBs with (a) bare electrode, (b) LCO-coating protection, and (c) LCO+CB-coating protection after 200 cycles.

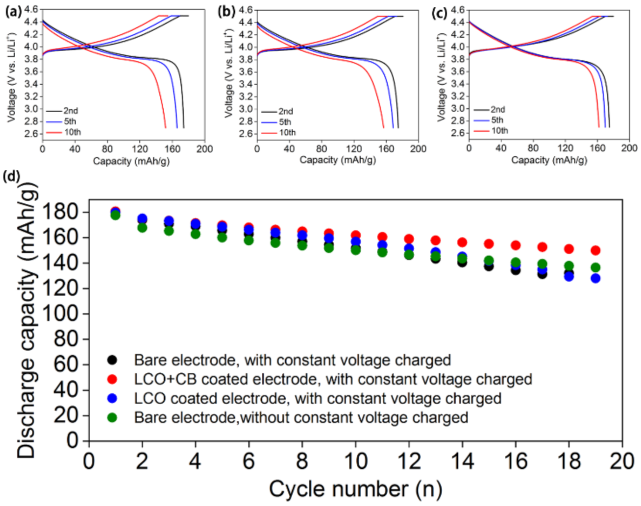

Fig. S14 Charge/discharge profiles of ASSLBs with (a) bare LiCoO2 electrode, (b) LCO-coating protection electrode, and (c) LCO+CB-coating protection electrode at 0.2 C and 60 oC with constant voltage charge step. (d) Comparison of discharge capacity of ASSLBs with different electrodes.

Table S1. Comparisons of dry polyethylene-based SPE all-solid-state $LiCoO_2$ batteries performance

Testing temperature [ºC]	Charge voltage cut-off [V]	Discharge capacity at 1st cycles [mAh/g]	Discharge capacity at different cycles [mAh/g, cycle number]	Average capacity decay per cycles (mAh/g)	Refs.
80	4.45	172.8	67, 75	1.4	[1]
80	4.2	148	124, 30	0.8	[2]
60	4.4	172	101, 100	0.71	[3]

60	4.4	174	134, 20	2	[4]
25	4.2	146	120, 30	0.87	[5]
80	4.2	120	/	/	[6]
60	**4.5**	**177**	**110.4, 100**	**0.56**	**This work**

Note: The capacity decay is calculated based on the second cycle capacity.

Reference

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