Supporting Information

for

Probing the Degradation of $LiCoO_2$ in Batteries Subjected to High-Voltage Cycling with ^{17}O Solid-state NMR Spectroscopy

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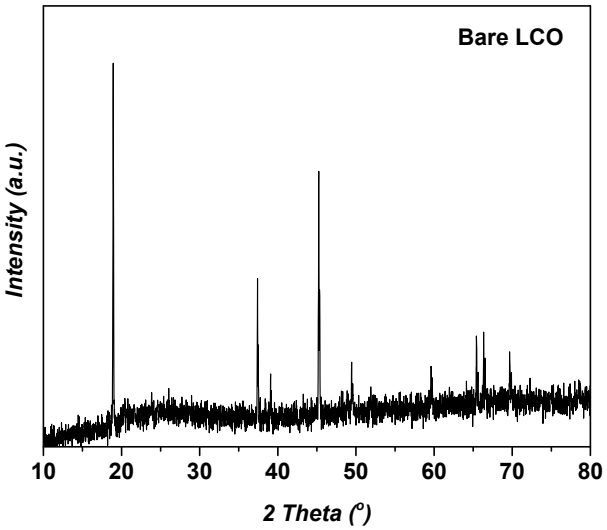

Figure S1. XRD pattern of bare LCO.

As shown in Figure S1, all the diffraction peaks can be attributed to the layered α-$NaFeO_2$ with $R\bar{3}m$ space group.

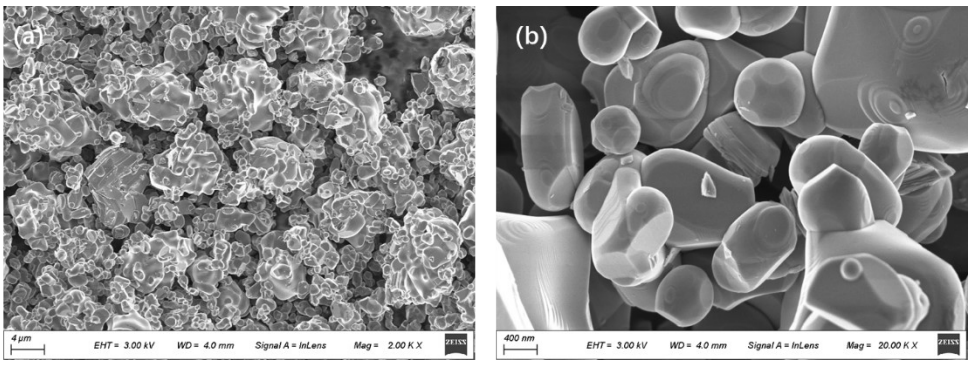

Figure S2. The SEM images of bare LCO at low (a) and (b) high magnification, respectively.

The scanning electron microscopy (SEM) images confirm that the size of LCO particles is 4-8 μm with a smooth surface. The electrochemical studies (Figure S3) performed in Li/LCO liquid half cells also give similar profile as for traditional LCO cathodes.

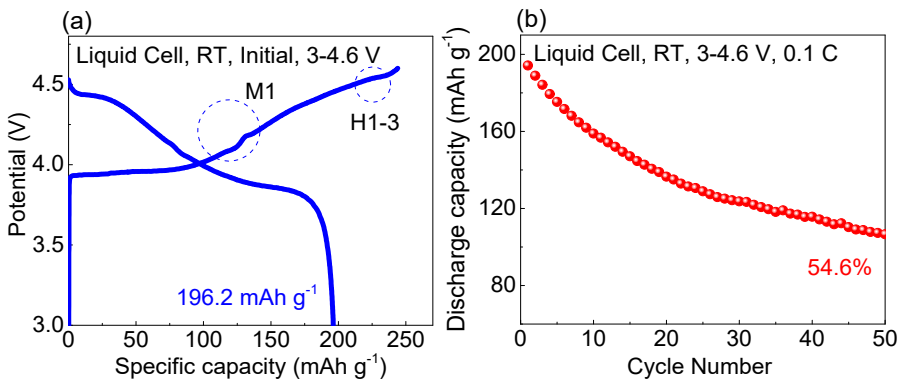

Figure S3. Initial cycle charge-discharge voltage profiles (a) and corresponding cycling performance of

Li/LCO liquid half-cells at cut-off potentials of 4.6–3.0 V vs. Li/Li^+ and a current density of 0.1 C.

The initial cycle charge/discharge curves of ^{17}O-labeled LCO in Figure S3 (a) show a discharge capacity of 196.2 mAh g^{-1} when cycling at the current density of 0.1 C and a cutoff potential of 4.6 V. The charging profile shows a long plateau at 3.9 V, two small plateaus at around 4.15 V, and a small plateau above 4.5 V, which respectively corresponds to the O3(I)/O3(II) phase transition, disorder/order transition associated with the monoclinic phase O3(M), and the O3(III)/H1-3 phase transition. At a cutoff voltage of 4.6 V, the LCO electrodes suffers from capacity loss with a capacity retention of 54.6% after 50 cycles.

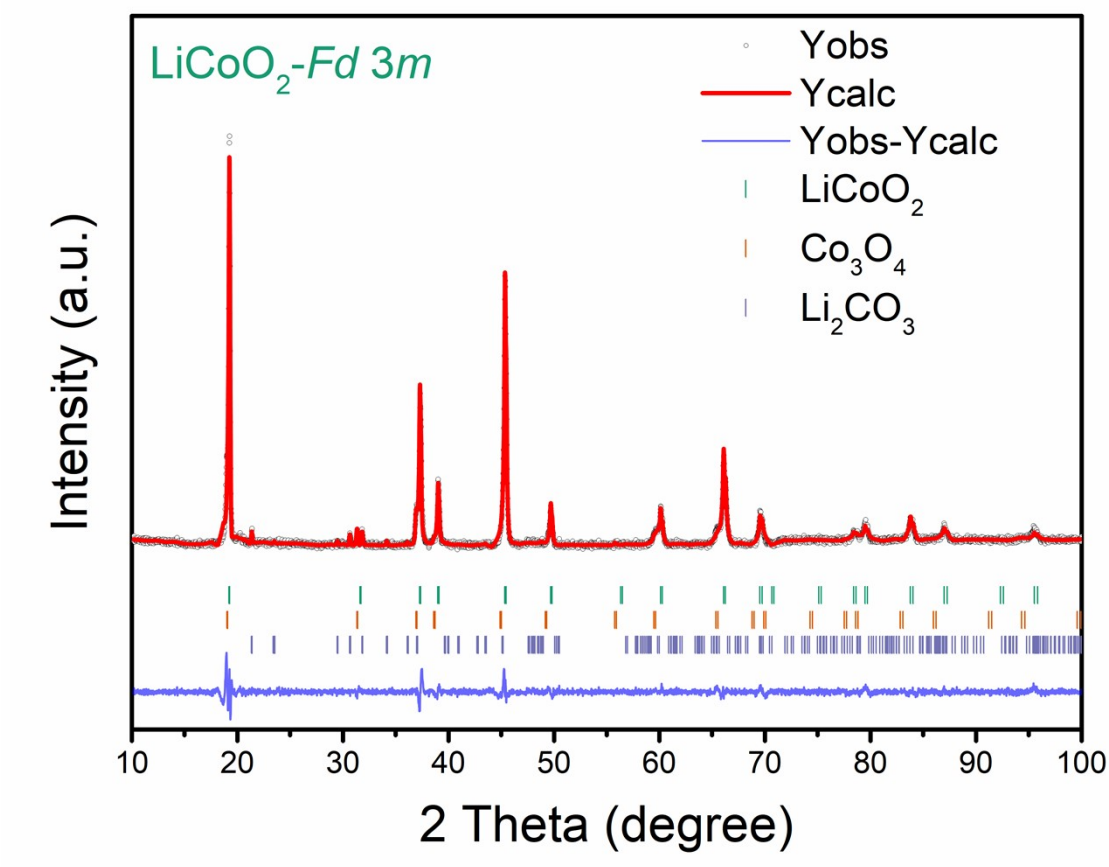

Figure S4. The (XRD) X-ray diffraction-Rietveld refinement of LT-LCO sample.

Table 1. Phase composition as determined from Rietveld refinement.

Samples	**Lattice parameters**							**Vol(Å^3)**	**Fraction(wt%)**	**R_p (%)**	**R_{wp} (%)**
	Space group	a(Å)	b(Å)	c(Å)	α(°)	β(°)	γ(°)				
$LiCoO_2$	$Fd3m$	7.99127	7.99127	7.99127	90	90	90	510.326	88.80(0.54)	2.07	3.03
Co_3O_4	$Fm\bar{3}m$	8.06765	8.06765	8.06765	90	90	90	525.100	1.81(0.06)	2.07	3.03
Li_2CO_3	C2/c	8.35501	4.97064	6.18612	90	114.68	90	233.445	9.40(0.44)	2.07	3.03

Table 2. Crystallographic parameters for the Rietveld refinement of LiCoO2 phase (space group: $Fd3m$) in LT-$LiCoO_2$.

$LiCoO_2$	**x**	**Y**	**Z**	**B**	**Mult**	**site**	**Occ**
O1	0.25289	0.00000	0.00000	0.500	32	32e	1.000
Li2	0.50000	0.50000	0.50000	0.794	16	16d	0.010
Li1	0.00000	0.00000	0.00000	0.570	16	16c	0.980
Co1	0.50000	0.50000	0.50000	0.794	16	16d	0.990
Co2	0.00000	0.00000	0.00000	0.570	16	16c	0.020

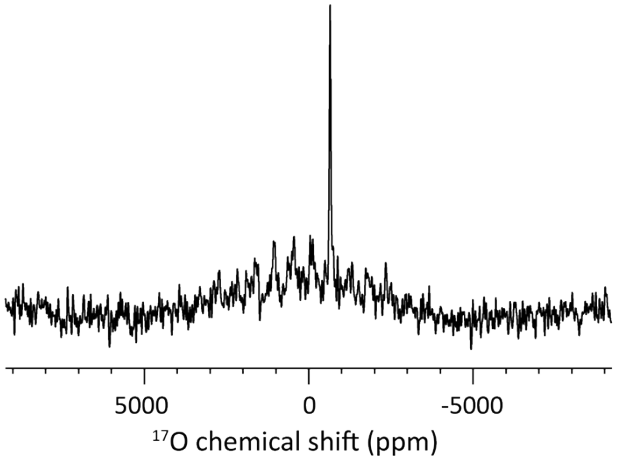

Figure S5. ^{17}O MAS NMR spectra of LT-$LiCoO_2$ sample.

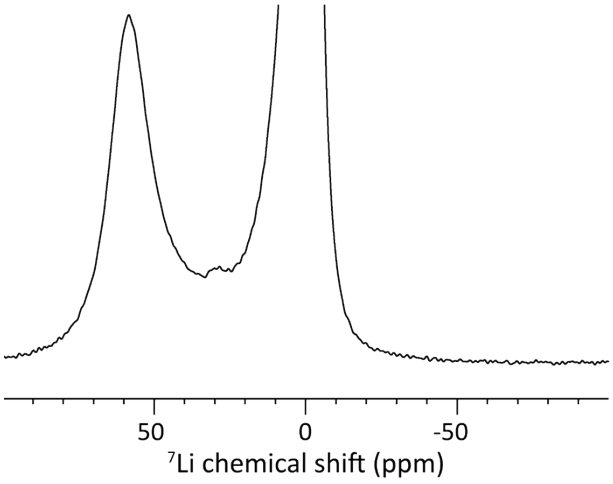

Figure S6. ^{7}Li MAS NMR spectra of LCO cathodes subjected to 50 cycles in liquid half-cells.

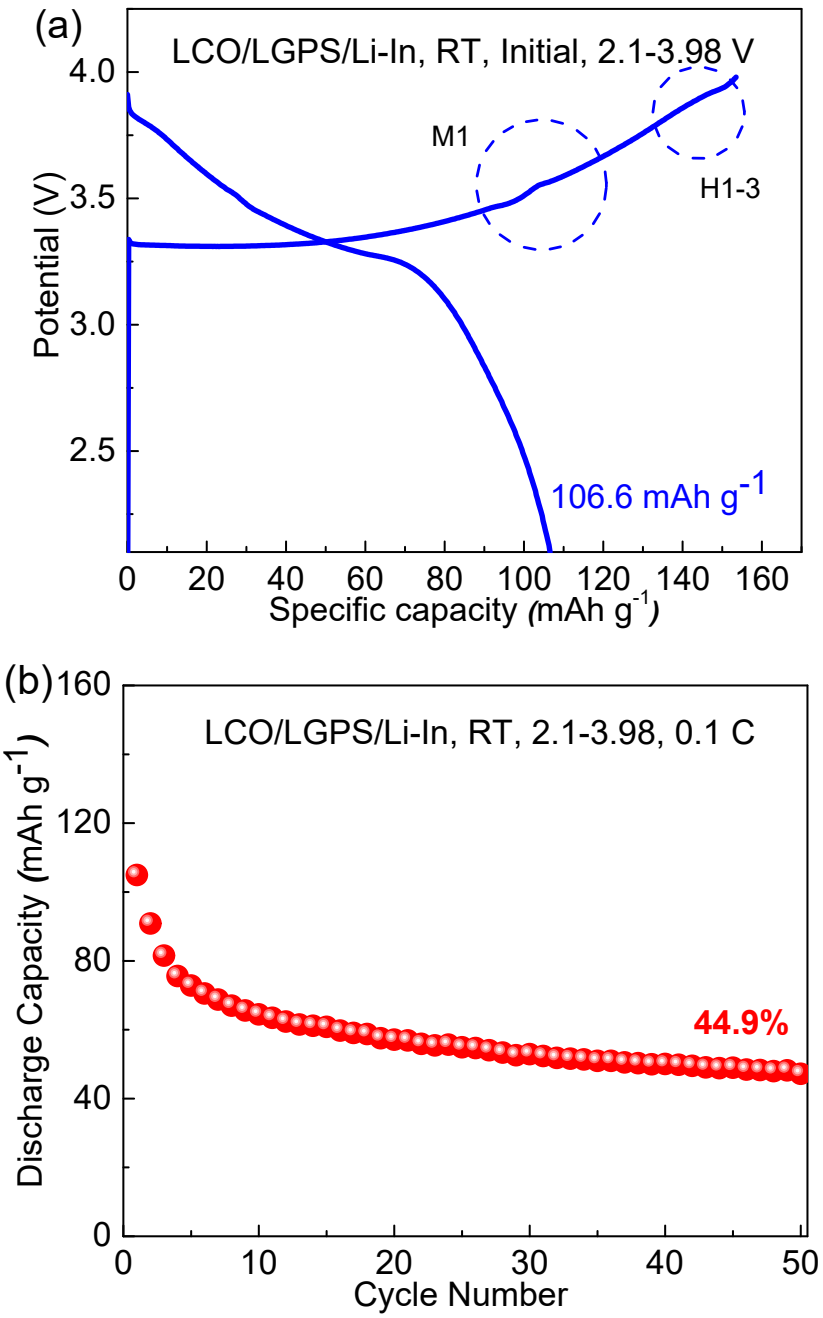

Figure S7. (a) First-cycle charge-discharge profile of LCO in LGPS-based ASSLBs. (d) The corresponding cycling performance at a current density of 0.1 C.

To probe the structural degradation of LCO in ASSLBs, $Li_{10}GeP_2S_{12}$ (LGPS)-based solid cells were cycled between 2.1 to 3.98 V vs. Li-In (corresponding to 2.72 - 4.6 V vs. Li^+/Li). The electrochemical performance of ^{17}O-labeled LCO in ASSLBs (Figure S5) is similar to that in liquid cells with a capacity retention of 45% after 50 cycles.

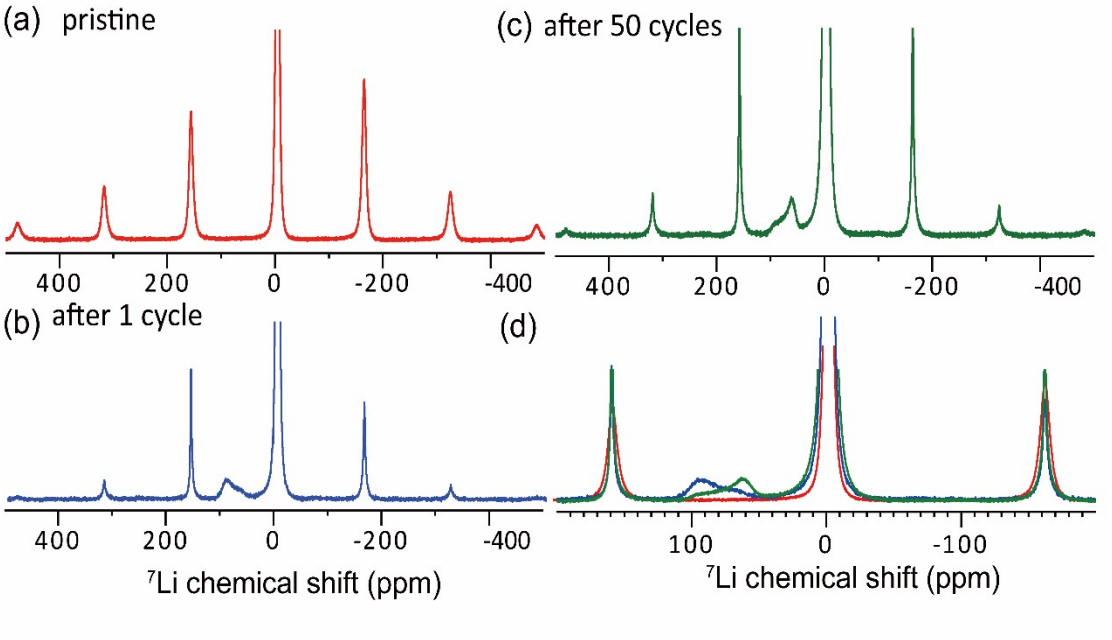

Figure S8. ^{7}Li MAS NMR spectra of LCO/LGPS composite cathodes at pristine state (a), after one cycle (b), and after fifty cycles (c). (d) Partial magnification of (b, c).

^{7}Li NMR spectra recorded on cycled electrode (Figure S8) shows that, in addition to the 0 ppm signal ascribed to the recovered O3 phase, residual weak signals located at 92.1 and 61.6 ppm can be observed. As discussed in previous work[1], these two signals can be attributed to lithium atoms in O3-type environment of O3(II) and O3(III) phases. The difference of chemical shift within the two phases is in fact due to both different degree of electronic delocalization and local atomic geometries, which often can be correlated with the evolution of c lattice parameter.[2-4] It is interesting to note that ^{7}Li NMR spectra of the electrode recovered from 50 cycles shows the same feature as for the electrode recovered from the initial cycle, despite the fact that the relative intensity of two phases is reversed. In other words, the signal of O3(III) phase may be accumulated after extended cycles due to irreversible phase transition.

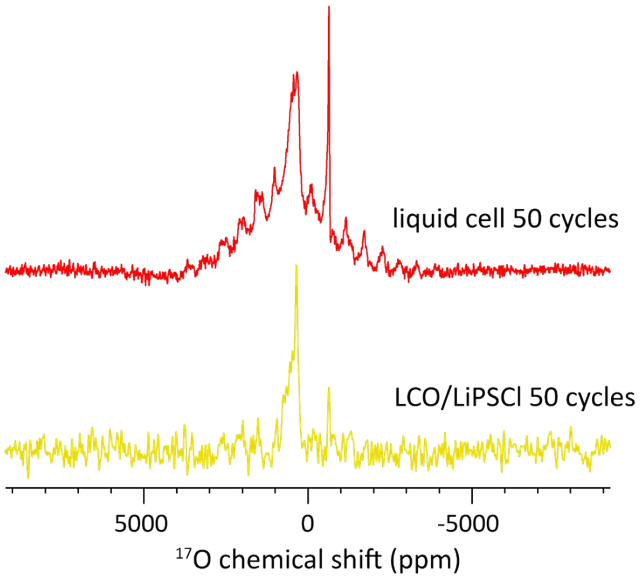

Figure S9. ^{17}O MAS NMR spectra of $LiCoO_2$ electrodes subjected to fifty charge-discharge cycles in liquid cells and LPSCl-based ASSLBs. The current density and the voltage window were under 4.6 (vs. Li^+/Li) and 3.98 V (vs. Li-In), respectively.

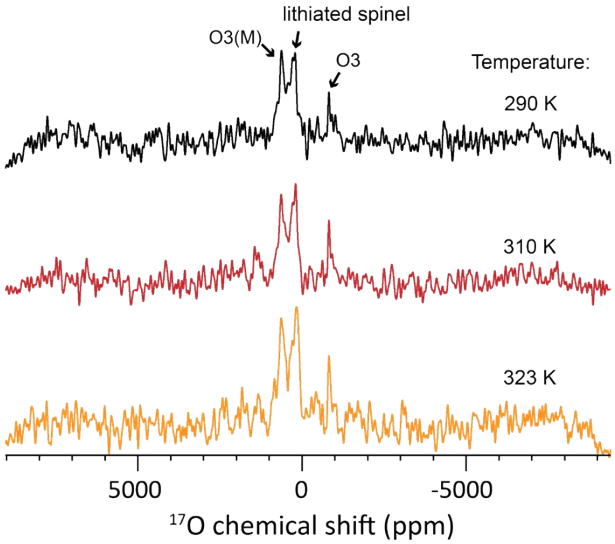

Figure S10. Variable-temperature ^{17}O MAS NMR spectra of LCO/LPSCL composite cathodes subjected to 50 cycles in ASSLBs at cut-off potentials of 2.1 to 3.98 V. Note that partial monoclinic phase (M1) also exists in this cycled sample.

Reference

1. J. Wan, J. Zhu, Y. Xiang, G. Zhong, X. Liu, Y. Li, K. H. L. Zhang, C. Hong, J. Zheng, K. Wang and Y. Yang, J. Energy Chem., 2021, 54, 786-794.
2. F.-E. Er-Rami, M. Duffiet, S. Hinkle, J. Auvergniot, M. Blangero, P.-E. Cabelguen, K. Song, F. Weill, C. Delmas and D. Carlier, *Chem. Mater.*, 2022, **34**, 4384-4393.
3. F. Geng, M. Shen, B. Hu, Y. Liu, L. Zeng and B. Hu, *Chem. Commun. (Camb)*, 2019, **55**, 7550-7553.
4. K. Shimoda, M. Murakami, D. Takamatsu, H. Arai, Y. Uchimoto and Z. Ogumi, *Electrochim. Acta*, 2013, **108**, 343-349.