Electronic Supplementary Information

Lithium bis(oxalate)borate additive in electrolyte to improve Li-rich layered oxide cathode materials

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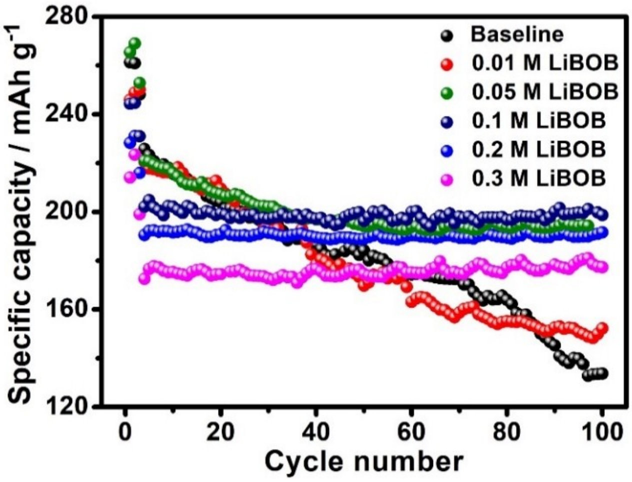

Figure S1: Cycling performance of LLO cells with various concentrations of LiBOB.

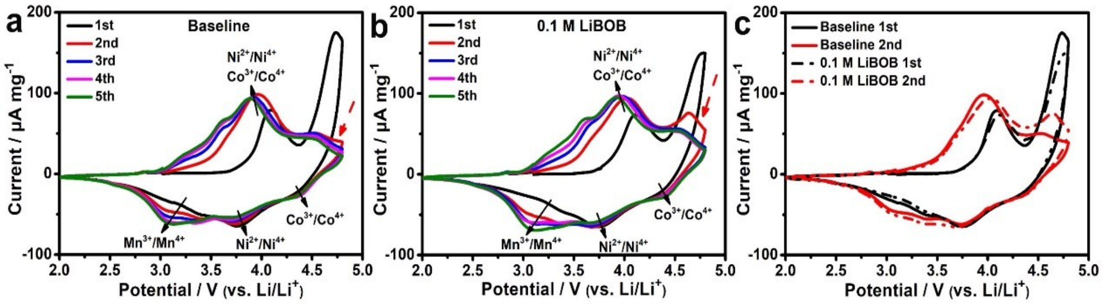

Figure S2: CV curves of LLO half cells (a) in baseline and (b) 0.1 M LiBOB electrolytes. (c) The comparison of initial two cycles.

As shown in Fig. S2c, the current of the peak at 4.5 V of anionic oxygen redox in the first cycle with 0.1 M LiBOB relatively decreased as compared with that in baseline counterpart and there is still an apparent oxygen redox peak during second cycle, indicating the inhibition impact of LiBOB on the activation of Li_2MnO_3 phase.

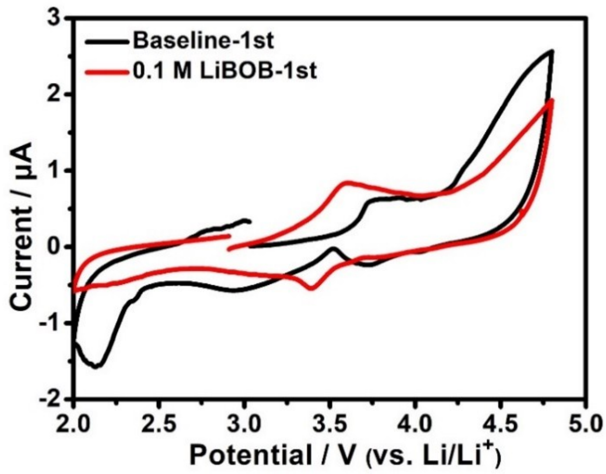

Figure S3: The CV curves of Li|Al cells in baseline and 0.1 M LiBOB electrolytes.

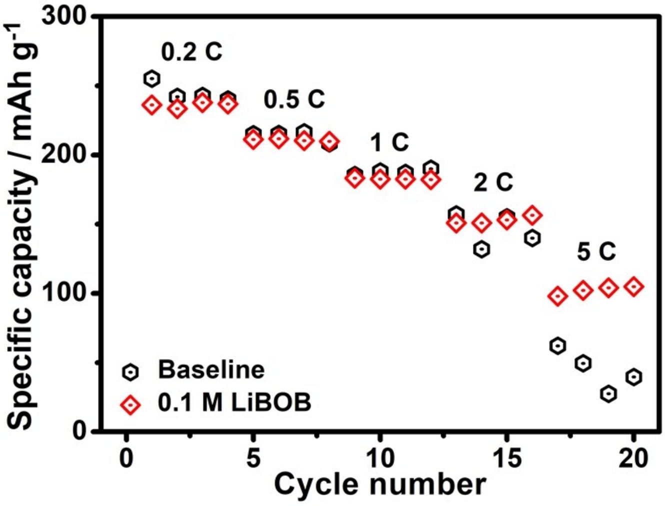

Figure S4: Rate performance of LLO in baseline and LiBOB-containing electrolytes.

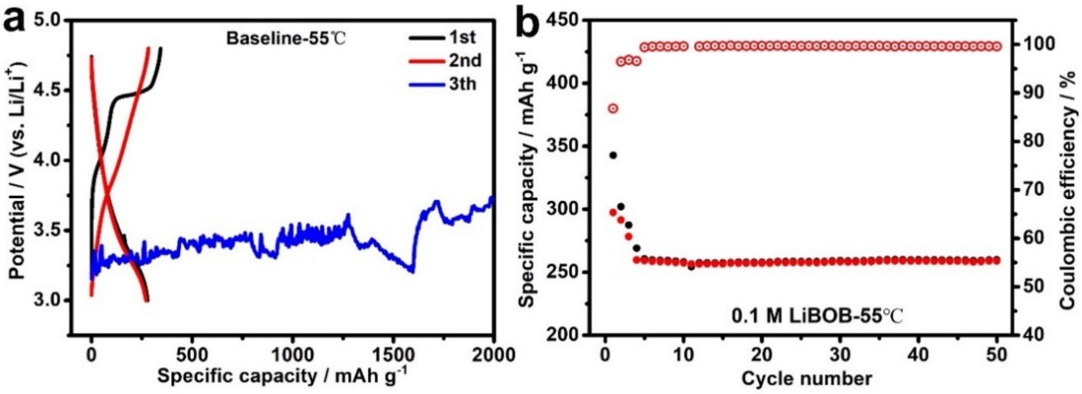

Figure S5: (a) The initial three-cycles charge/discharge profiles of battery with baseline electrolyte at 55℃. (b) The cycling performance of cell with 0.1 M LiBOB at 55℃.

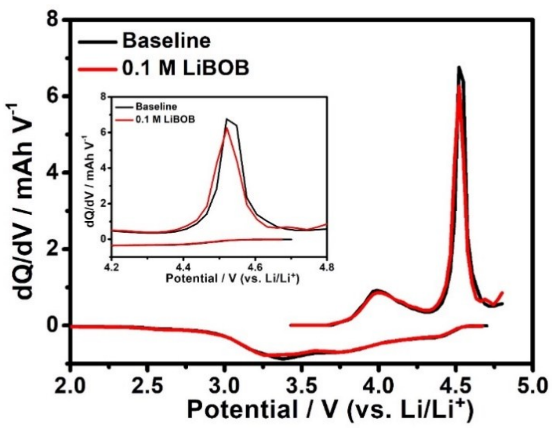

Figure S6: The dQ/dV profiles in baseline and LiBOB-containing electrolytes during the first cycle at 0.1C.

The differential capacity curves display that the peak at about 4.5 V shifts to a slightly lower voltage along with a weaken intensity in 0.1 M LiBOB electrolyte, revealing the preferential oxidation of LiBOB,[1] which is consistent with Fig. S3.

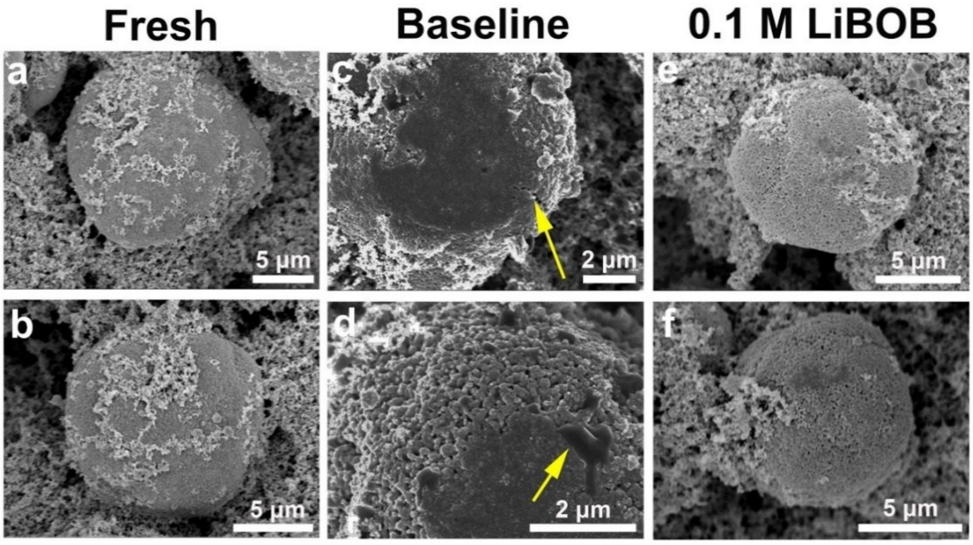

Figure S7: SEM micrographs of (a, b) the fresh LLO cathode and the cathode after cycling (c, d) in baseline and (e, f) 0.1 M LiBOB electrolytes.

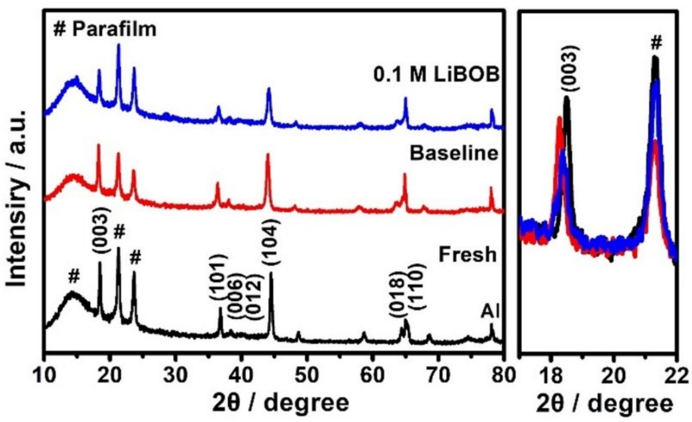

Figure S8: XRD patterns of fresh and cycled LLO cathodes with baseline and 0.1 M LiBOB electrolytes.

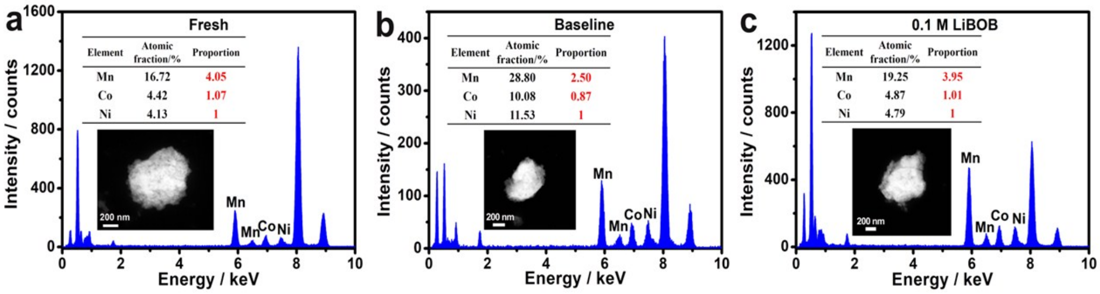

Figure S9: EDS spectra of (a) fresh LLO cathode and cycled cathodes (b) in baseline and (c) 0.1 M LiBOB electrolytes. Insets in (a-c) are the selected region for the EDS measurement and the corresponding proportion of Mn, Co and Ni elements.

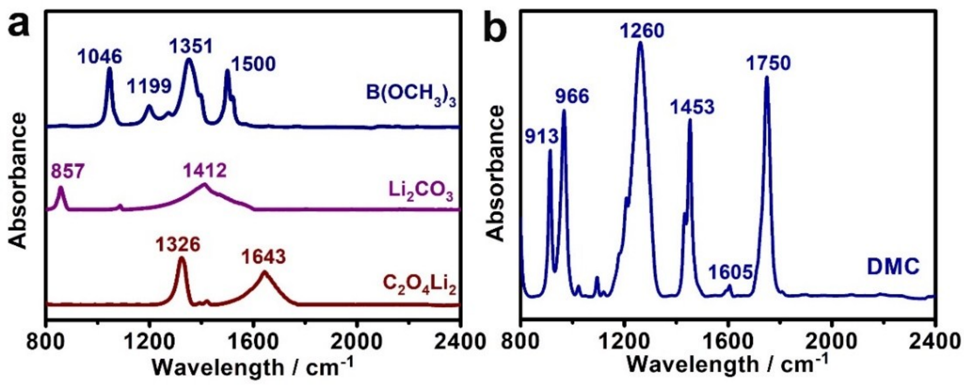

Figure S10: Individual FTIR spectra of (a) Li_2CO_3, $C_2O_4Li_2$, $B(OCH_3)_3$ and (b) DMC.

Table S1: Calculated vibration frequencies and assignments of 1B-O structure according to DFT calculation.

Calculated ν (cm^{-1})	Observed ν (cm^{-1})	Assignments
1869.3	**1823**	**C=O asymmetric stretching**
1837.3	**1778**	**C=O symmetric stretching**
1243.8	**1226**	**O-C-C asymmetric stretching**
941.0	**987**	**O-B-O asymmetric stretching**

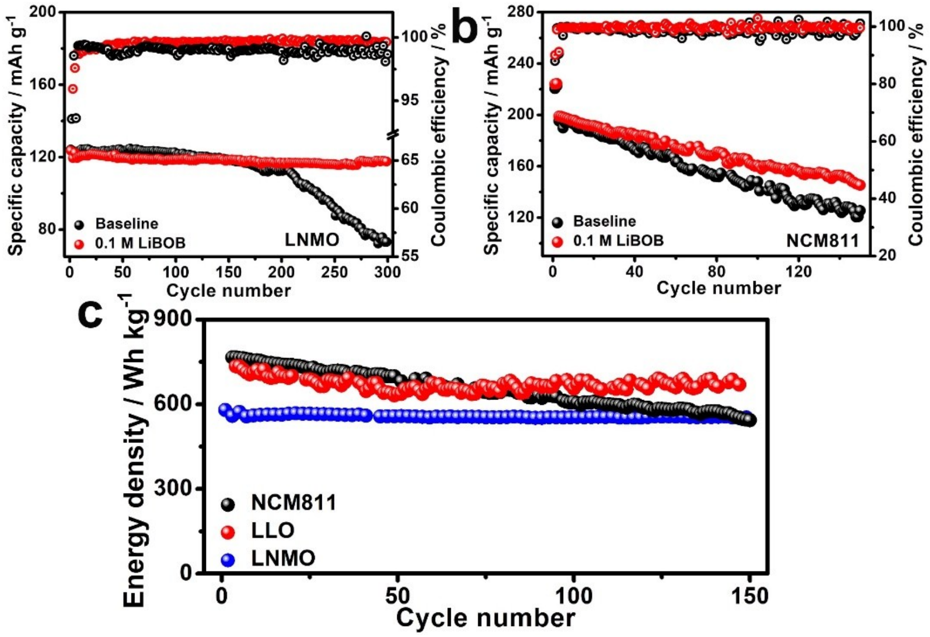

Figure S11: The cycling performances of (a) Li|$LiNi_{1.5}Mn_{0.5}O_4$ and (b) Li|$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ half-cells at 1 C with different electrolytes. (c) The energy densities of Li|LLO, Li|NCM811 and Li|LNMO coin cells at 0.5 C in 150 cycles.

In addition to the LLO materials, the LiBOB additive also plays a noteworthy role in other high-voltage cathodes such as $LiNi_{0.5}Mn_{1.5}O_4$ and Ni-rich electrodes.[2-6] We measured the cycling performance of Li|$LiNi_{0.5}Mn_{1.5}O_4$ and Li|$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ half-cells at 1 C in the voltage range of 3.0-4.9 V and 3.0-4.7 V, respectively (Fig. S11a, S11b). Obviously, moderate LiBOB could also extend the service life of LNMO and NCM811. Moreover, as shown in Fig. S11c, LLO cathode presents the highest and most stable energy density compared with Li|NCM811 and Li|LNMO cells in 0.1 M LiBOB electrolyte, further highlighting the positive effect of LiBOB additive in LLO cathode.

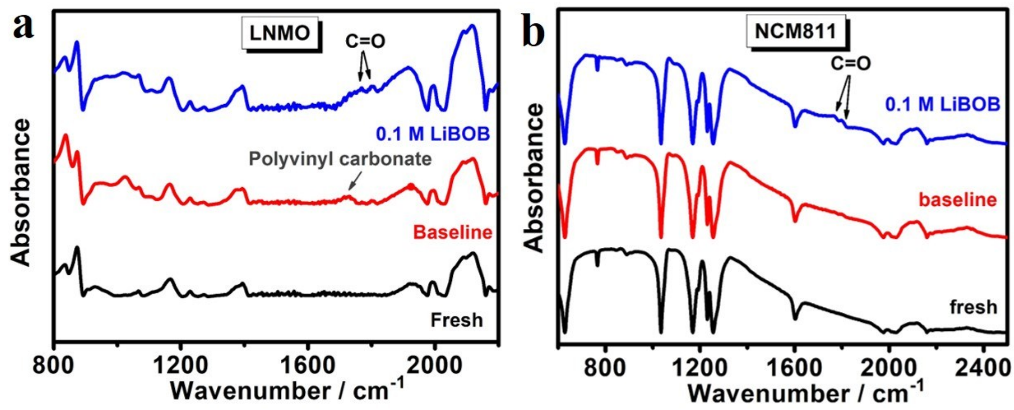

Figure S12: FTIR spectra of fresh and cycled (a) LNMO electrode at 3.0-4.9 V and (b) NCM811 electrode at 3.0-4.7 V.

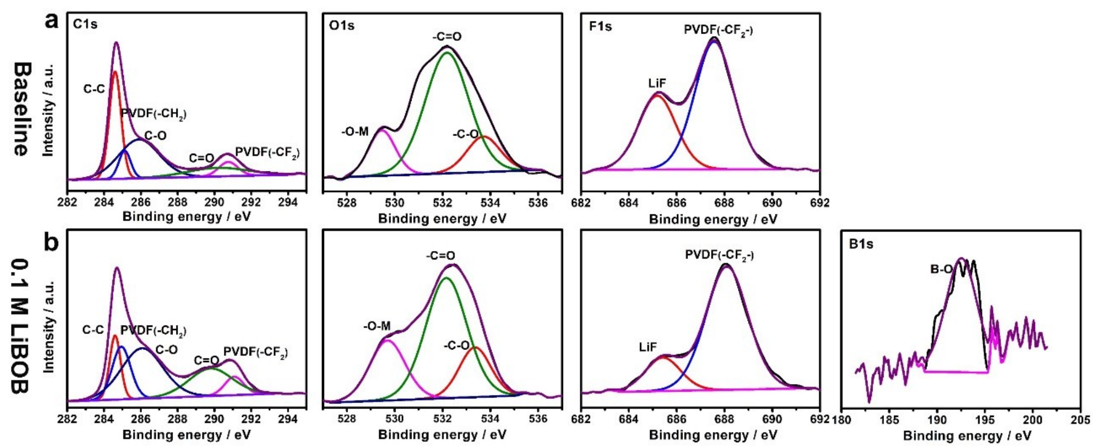

Figure S13: XPS characterization of $Li_{1.2}Mn_{0.54}Co_{0.13}Ni_{0.13}O_2$ electrode after 100 cycles (a) in baseline and (b) 0.1 M LiBOB electrolytes.

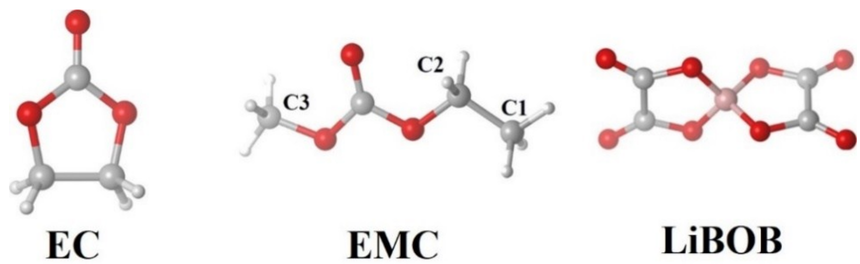

Figure S14: The Optimized structures of EC, EMC and BOB^-.

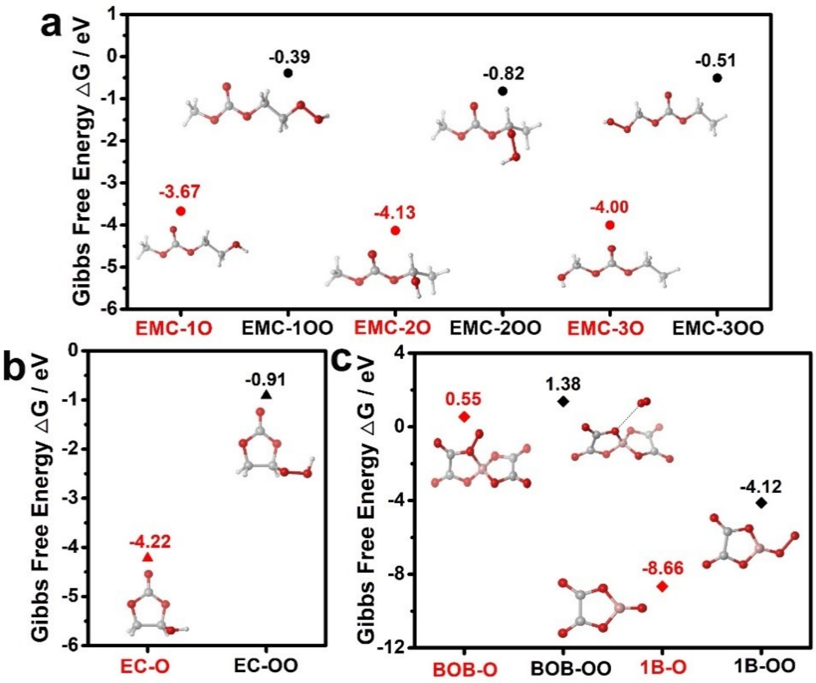

Figure S15: The Gibbs free energies of the active oxygen species ($O_2^{\cdot-}$/$O^{\cdot-}$) with (a) EMC, (b) EC and (c) LiBOB, respectively.

Since EMC owns three distinct positions of carbon (defined as C1, C2 and C3, Fig. S14) and LiBOB has various decomposition modes, which complicate their style of connection with oxygen radicals ($O_2^{\cdot-}$/$O^{\cdot-}$), the Gibbs free energy (ΔG) calculations were performed to obtain the optimal combinations of EC, EMC and LiBOB with oxygen. As displayed in Fig. S15a, when oxygen radicals combine with C2 in EMC, the lowest Gibbs free energy appears. Differently, there is only one position of carbon atom in EC, which bonds with the oxygen species (Fig. S15b). It can be seen in Fig. S15c that the partially decomposed structure of BOB^- tends to trap oxygen radicals in priority as compared with the unreacted BOB^-.

References

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