Supporting Information

Operando Observation of Lithiation and Delithiation Reactions of a LiCoO2 -Li3BO3 Composite Electrode Formed on a Li6.6La3Zr1.6Ta0.4O12 Solid Electrolyte Sheet by Laboratory-based Hard X-ray Photoelectron Spectroscopy

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*Estimation of amount of LBO*

LBO is formed by mixing 10 μL of aqueous solutions saturated with LiOH and H3BO3, followed by annealing, according to the following chemical reaction:

The moles of LiOH (saturation solubility: ~5.22 mol/L) and H3BO3 (saturation solubility: ~0.94 mol/L)contained in the 10 μL of saturated aqueous solutions are 5.22 × 10-5 mol and 9.38 × 10-6 mol, respectively. Thus, the amount of Li3BO3 (79.634 g/mol) can be roughly estimated to be 9.38 ×10-6 mol (0.747 mg).

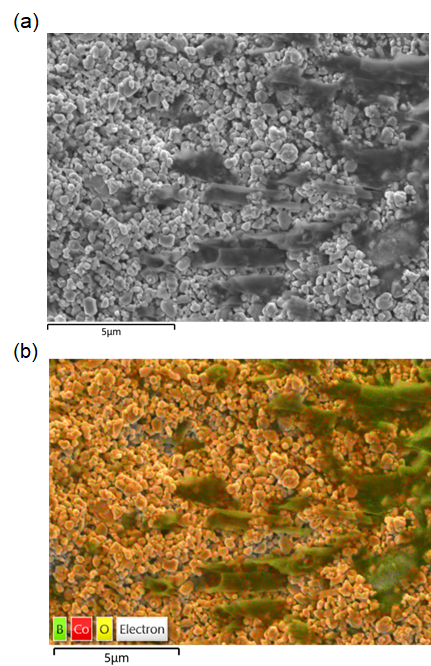


Figure S (a) A SEM image and (b) EDS map of LCO-LBO composite positive electrode in top view.

Figure S1 shows a SEM image and EDS map of the LCO-LBO composite positive electrode. The size of primary LCO particles is around 200 nm and those are interconnected by LBO distributed in the composite positive electrode

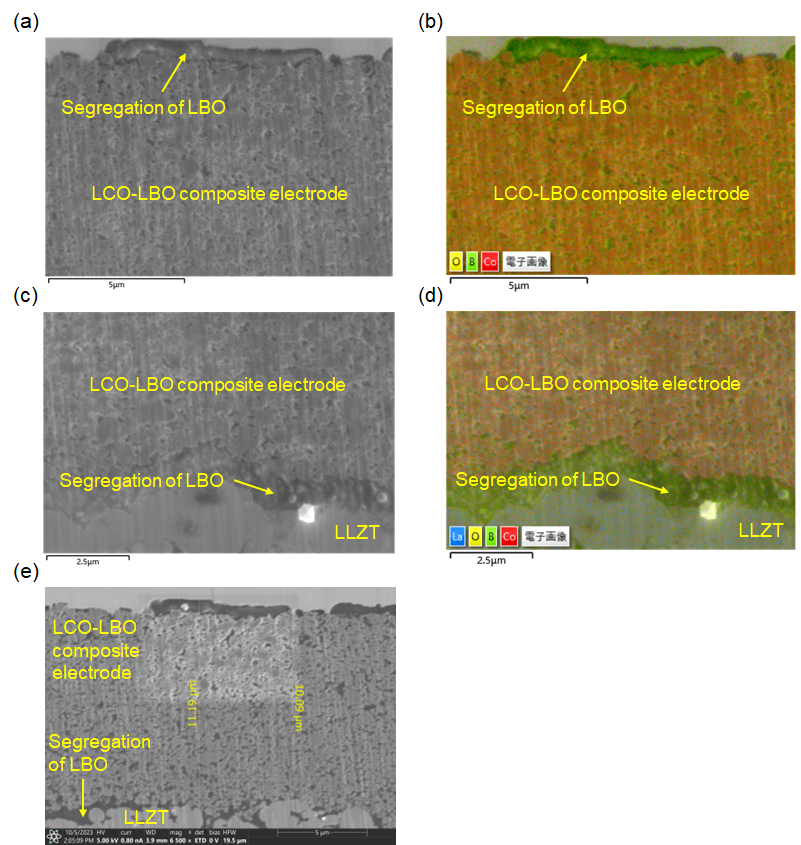


Figure S Cross-sectional (a, c, e) SEM images and (b, d) EDS maps of the LCO-LBO composite positive electrode. (a, b) The top side (outermost side), (c, d) bottom side (LLZT side) and (e) entire LCO-LBO composite electrode.

Figure S2 shows cross-sectional SEM images and EDS maps of the LCO-LBO composite positive electrode. LBO is well distributed in the entire composite electrode but some LBO is segregated on the top and bottom of the composite electrode.

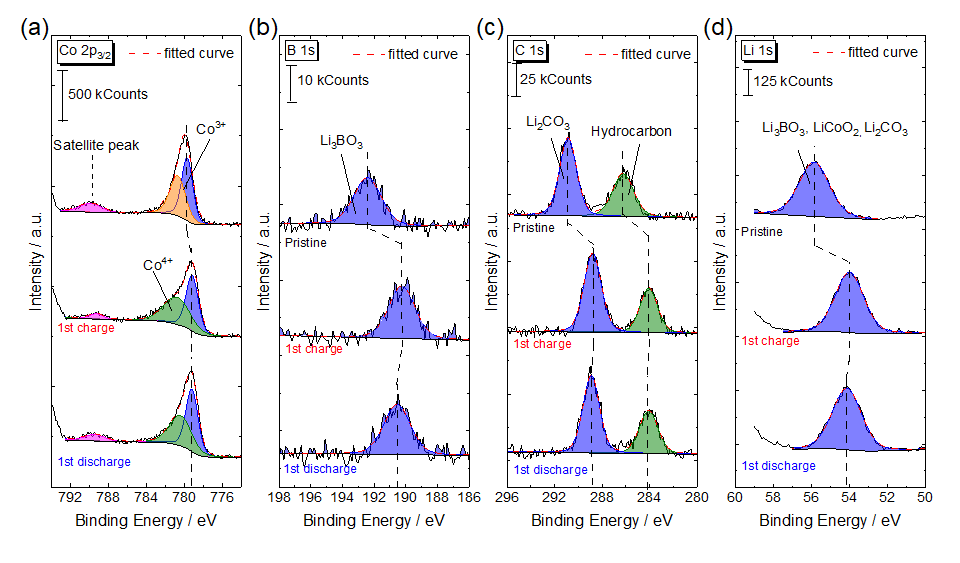


Figure S (a) Co 2p3/2, (b) B 1s, (c) C 1s, and (d) Li 1s photoelectron spectra of the LCO-LBO composite electrode before and after charge/discharge cycles without calibration.

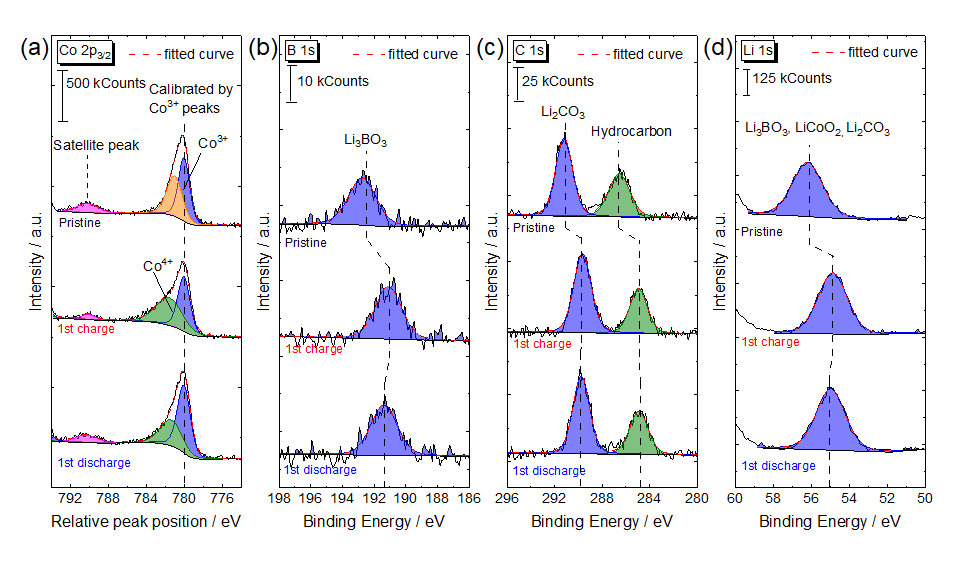


Figure S (a) Co 2p3/2, (b) B 1s, (c) C 1s, and (d) Li 1s photoelectron spectra of the LCO-LBO composite electrode before and after charge/discharge cycles with calibration using the Co 2p peak of LCO at 780.0 eV.

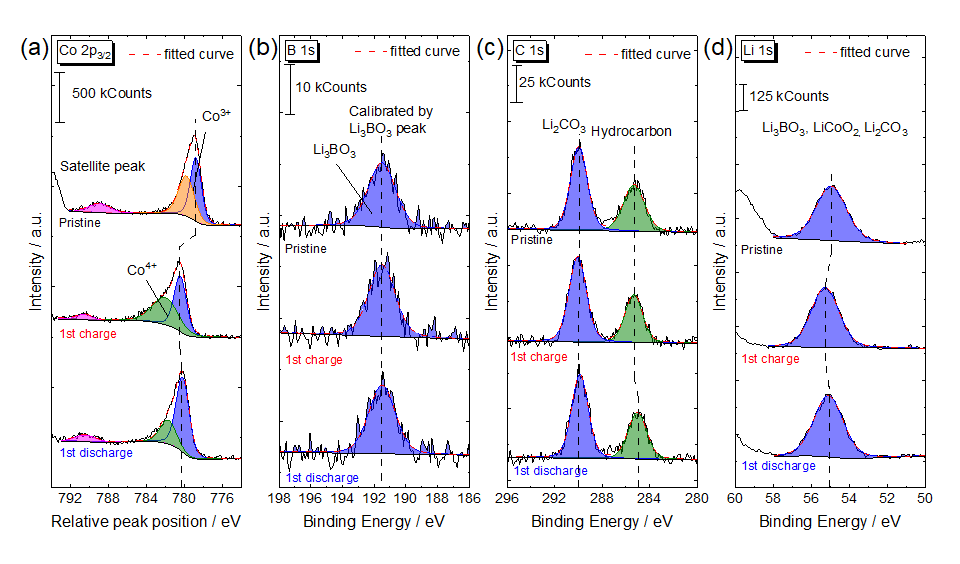


Figure S (a) Co 2p3/2, (b) B 1s, (c) C 1s, and (d) Li 1s photoelectron spectra of the LCO-LBO composite electrode before and after charge/discharge cycles with calibration using the B 1s peak of LBO at 191.5 eV.

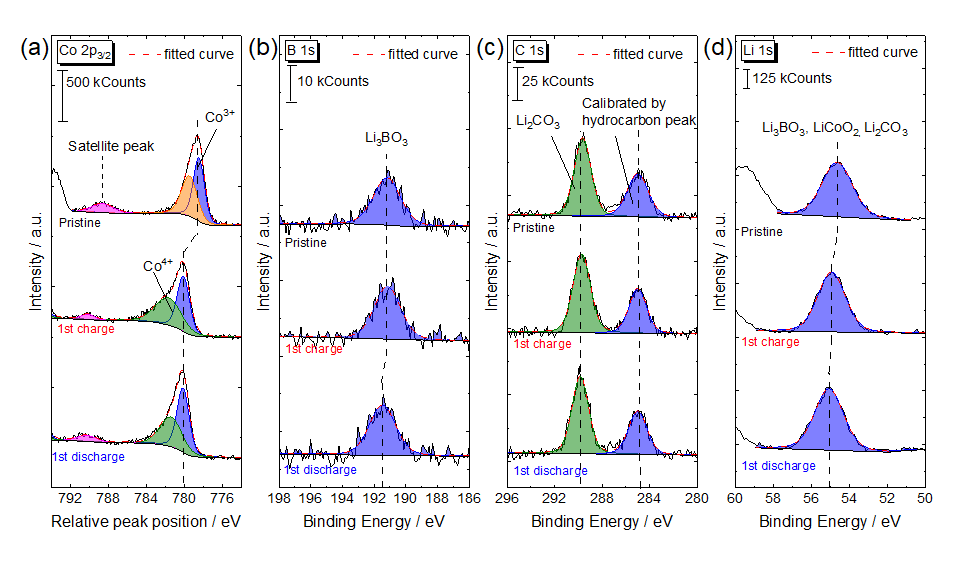


Figure S (a) Co 2p3/2, (b) B 1s, (c) C 1s, and (d) Li 1s photoelectron spectra of the LCO-LBO composite electrode before and after charge/discharge cycles with calibration using the C 1s peak of hydrocarbon at 285.0 eV.

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | **Without asymmetry** | **With asymmetry** |
| **Pristine** | Intensity / Counts | 3.03×104 | 3.05×104 |
| Peak position / eV | 192.41 | 192.41 |
| FWHM / eV | 2.05 | 2.048 |
| Asymmetry factor | 0.001 | 0.239 |
| Residue | 201.2838567 | 197.4717028 |
| **1st charge** | Intensity / Counts | 3.24×104 | 3.24×104 |
| Peak position / eV | 190.24 | 190.21 |
| FWHM / eV | 1.968 | 1.956 |
| Asymmetry factor | 0.001 | 0.175 |
| Residue | 173.1236171 | 170.7620849 |
| **1st discharge** | Intensity / Counts | 3.13×104 | 3.11×104 |
| Peak position / eV | 190.55 | 190.53 |
| FWHM / eV | 1.99 | 1.975 |
| Asymmetry factor | 0.001 | 0.083 |
| Residue | 240.825556 | 240.8535978 |

Table S1 Curve fitting results of photoelectron spectra in the B 1s region of LCO-LBO composite electrode.

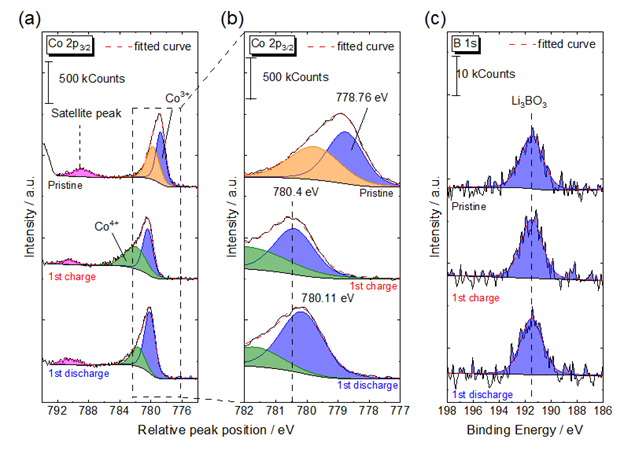


Figure S7 (a) Co 2p3/2 and (c) B 1s photoelectron spectra of the LCO-LBO composite electrode before and after charge/discharge cycles with calibration using the B 1s peak of LBO at 191.5 eV. (c) Magnified graphs of dashed box shown in (a).