Supplementary Information

Li-Modified $BaCoO_{3-\delta}$ for Thermochemical Energy Storage: Enhanced Reaction Performance and Modification Mechanism

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Table S1. Peak position data of BaO (ICCD PDF #04-005-4400)

2θ	d(Å)	I(f)	(h k l)
27.922	3.1928	100	(1 1 1)
32.352	2.765	83.4	(2 0 0)
46.405	1.9552	50.8	(2 2 0)
55.031	1.6674	35.9	(3 1 1)
57.701	1.5964	15.3	(2 2 2)
67.721	1.3825	6.2	(4 0 0)
74.77	1.2687	11.9	(3 3 1)
77.062	1.2366	15.2	(4 2 0)

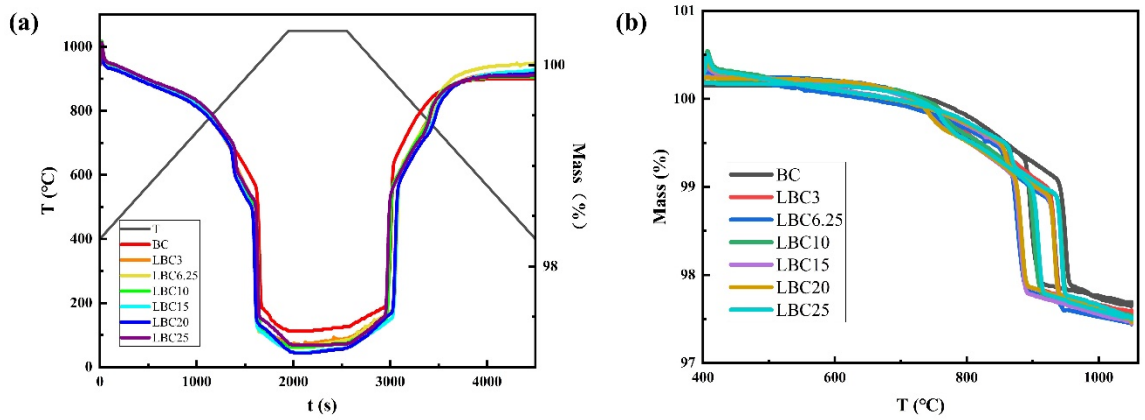
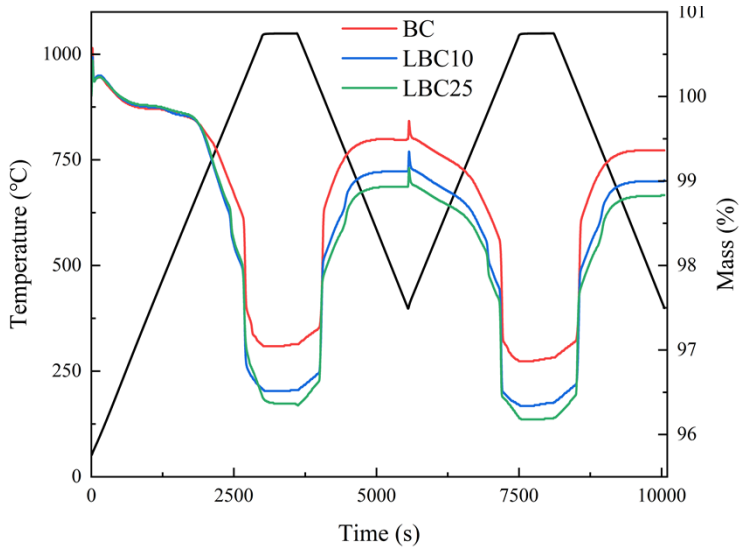


Figure S1. The raw TG data (a) and the thermogravimetric hysteresis curve (b) of $BaCoO_{3-\delta}$ and $Li_xBa_{1-x}CoO_{3-\delta}$;



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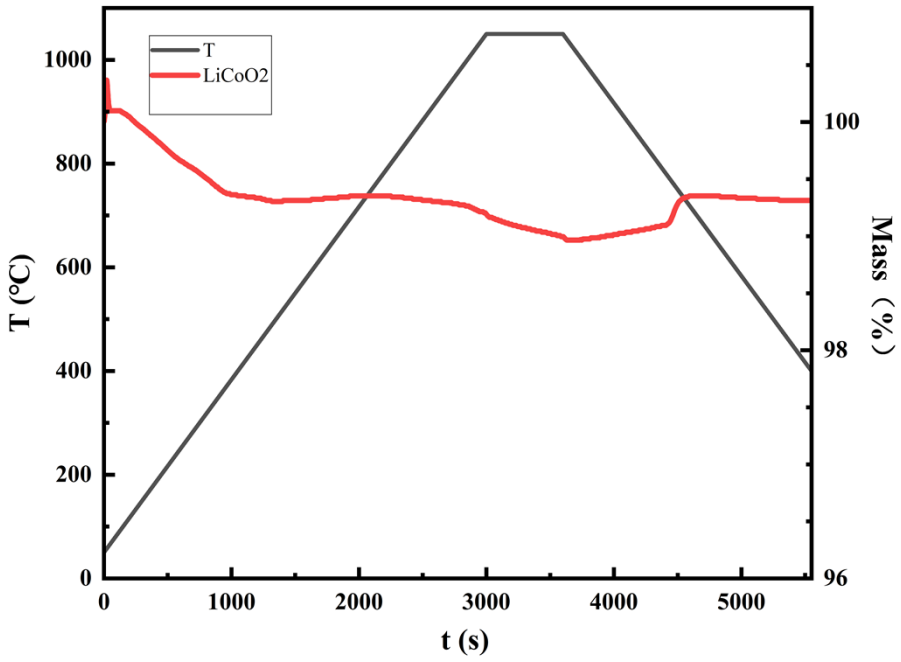
18 **Figure S2.** The TG results of two cycles for BC, LBC10, and LBC25;



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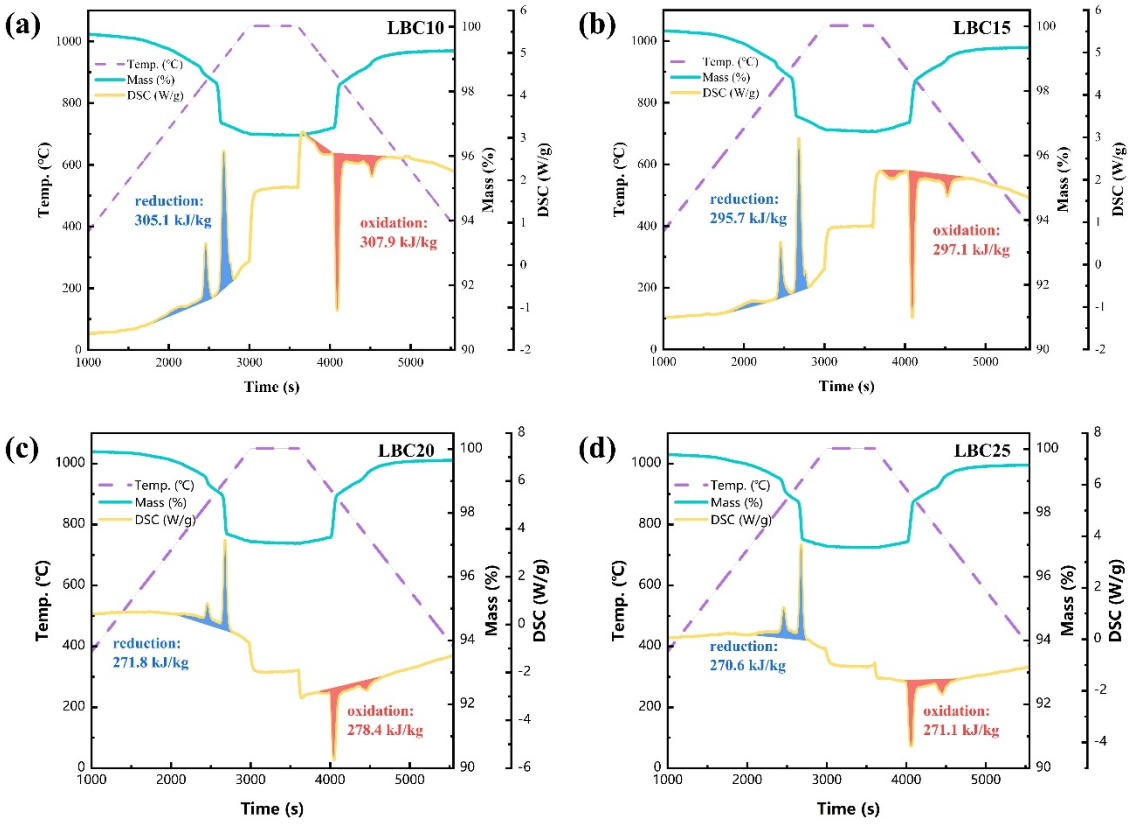
20 **Figure S3.** The TG results of $LiCoO_2$ sample;



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22 **Figure S4.** DSC results of the thermal storage performance: (a) LBC10; (b) LBC15; (c)

23 LBC20; (d) LBC25;

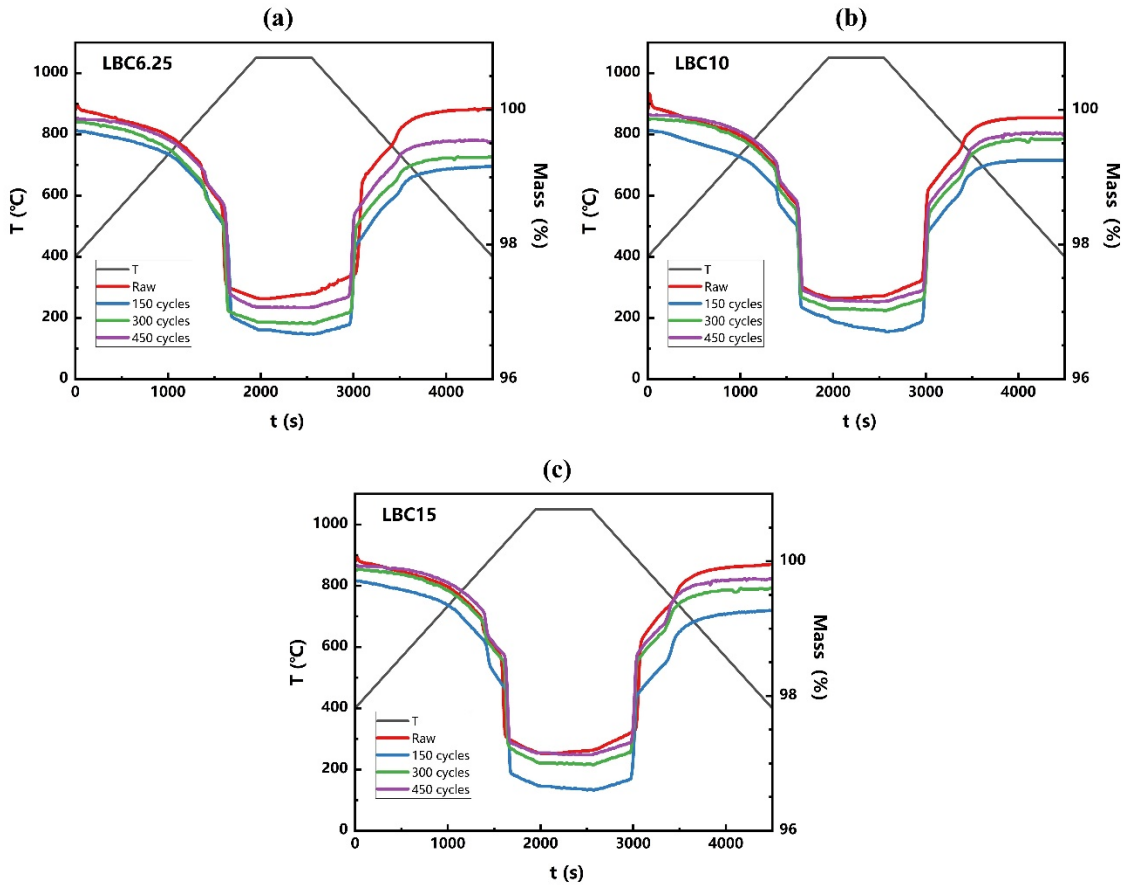
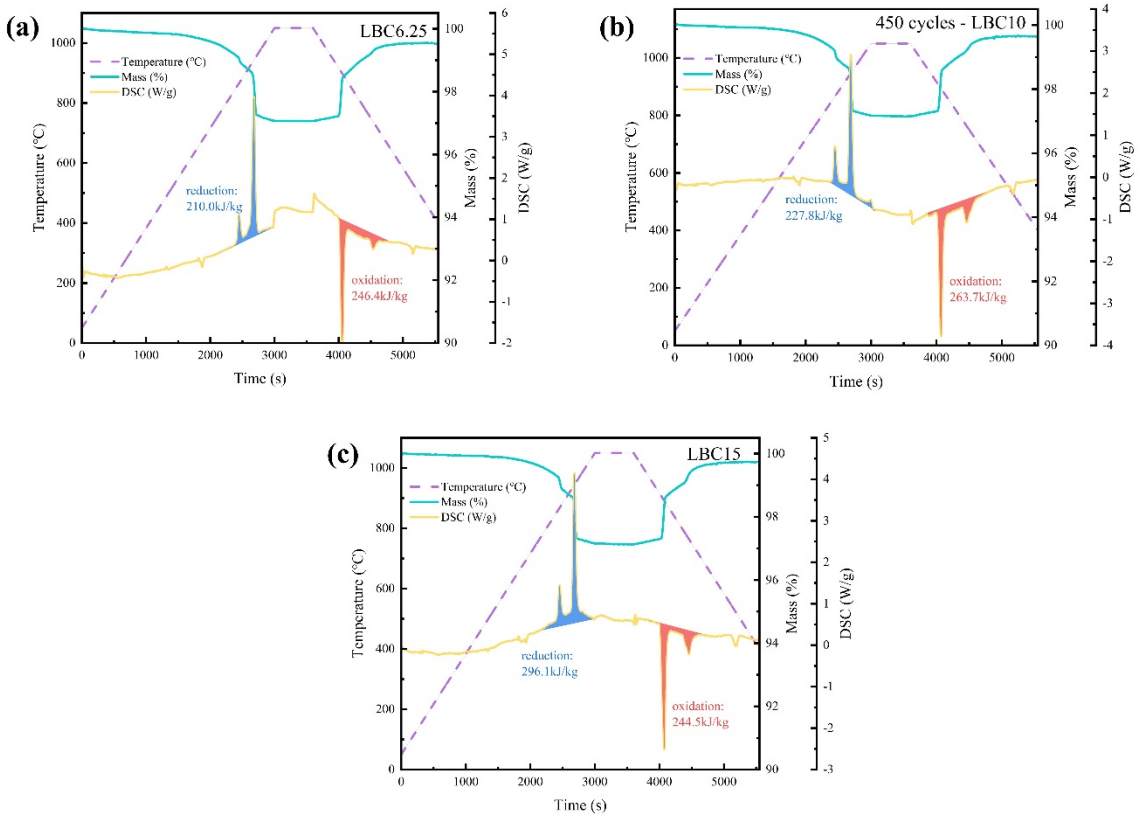


Figure S5. The raw TG data for the cyclic reactions: (a) LBC6.25; (b) LBC10; (c) LBC15;



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27 **Figure S6.** DSC results of the thermal storage performance after 450 cycles: (a) LBC6.25;

28 (b) LBC10; (c) LBC15;

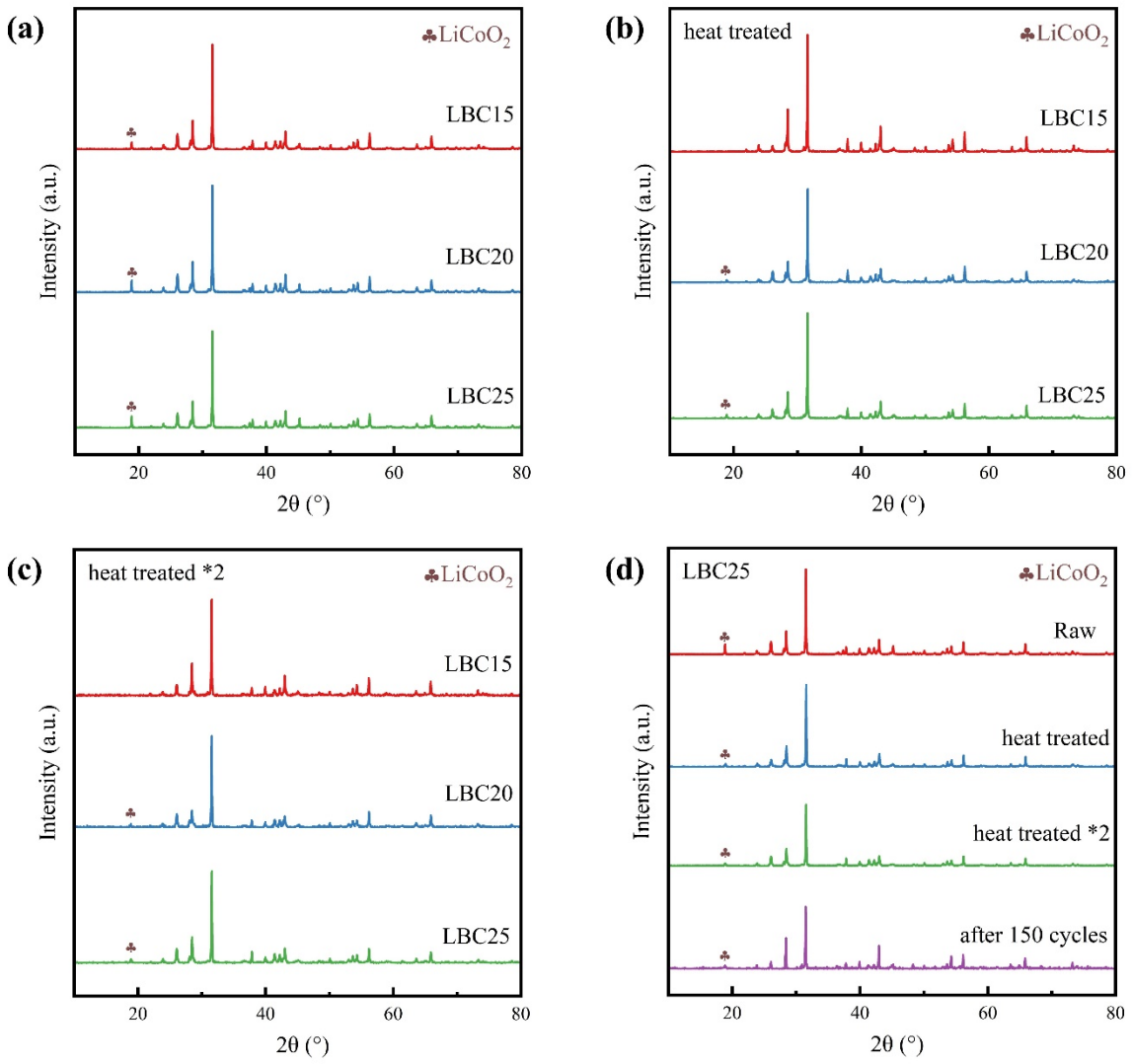

Figure S7. XRD patterns of LBC15, LBC20, and LBC25 before and after thermal treatment: (a) raw samples; (b) samples after thermal treatment; (c) samples after second thermal treatment; (d) comparison of LBC25 XRD patterns before and after thermal treatment and cycling tests.

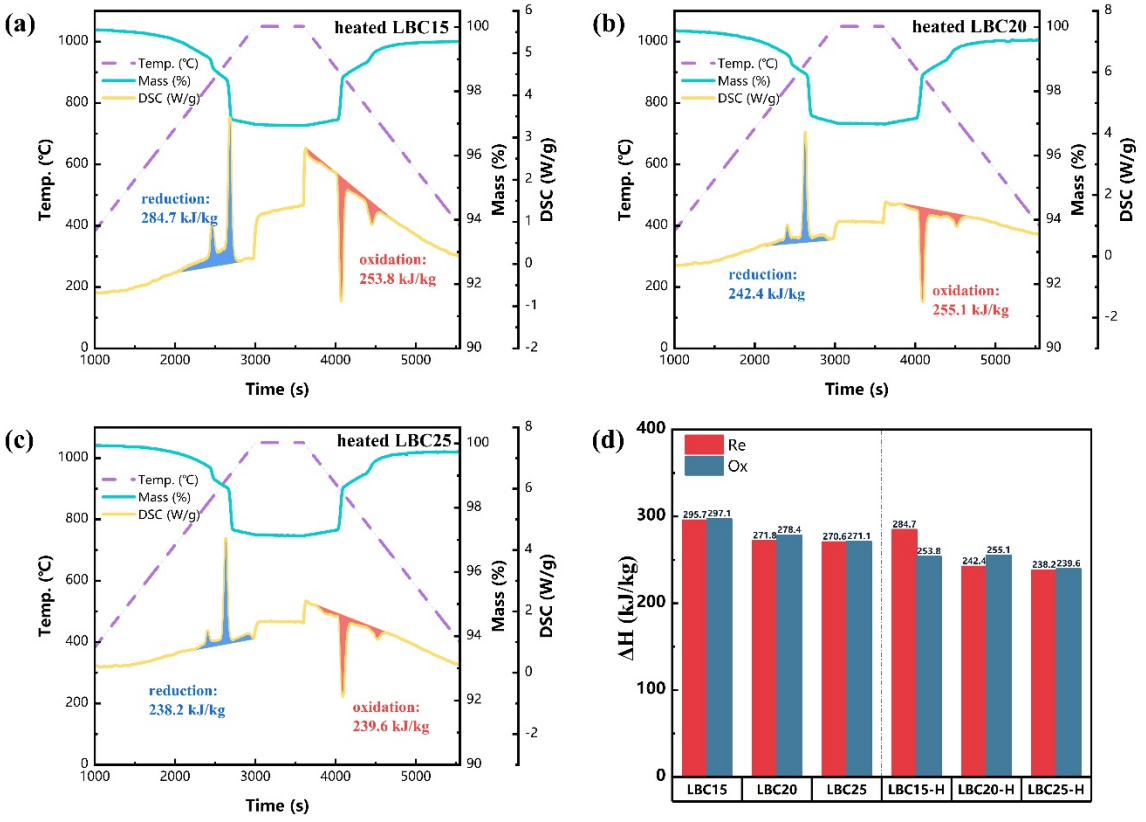

Figure S8. Thermochemical energy storage performance of samples after thermal treatment: (a) LBC15; (b) LBC20; (c) LBC25; (d) comparison of heat storage density before and after thermal treatment.

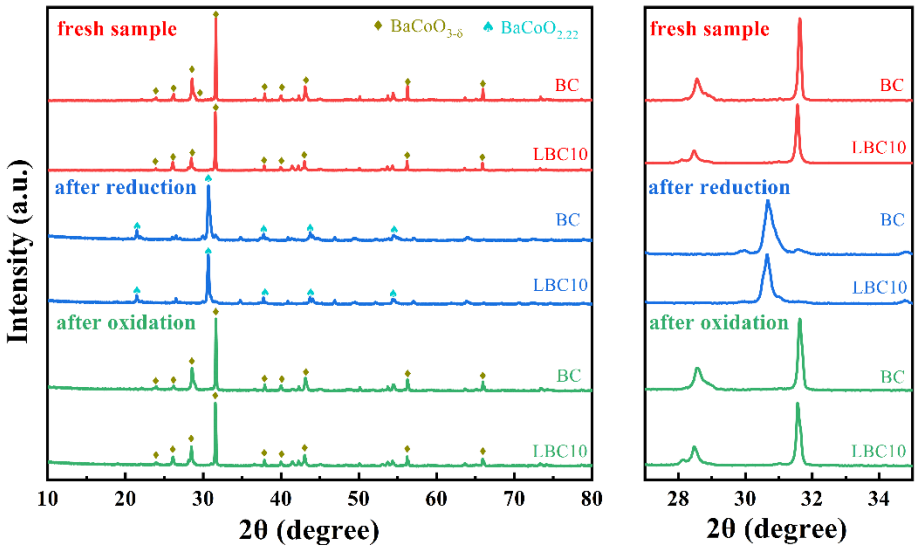

Figure S9. XRD patterns of BC and LBC10 before and after reduction and oxidation;

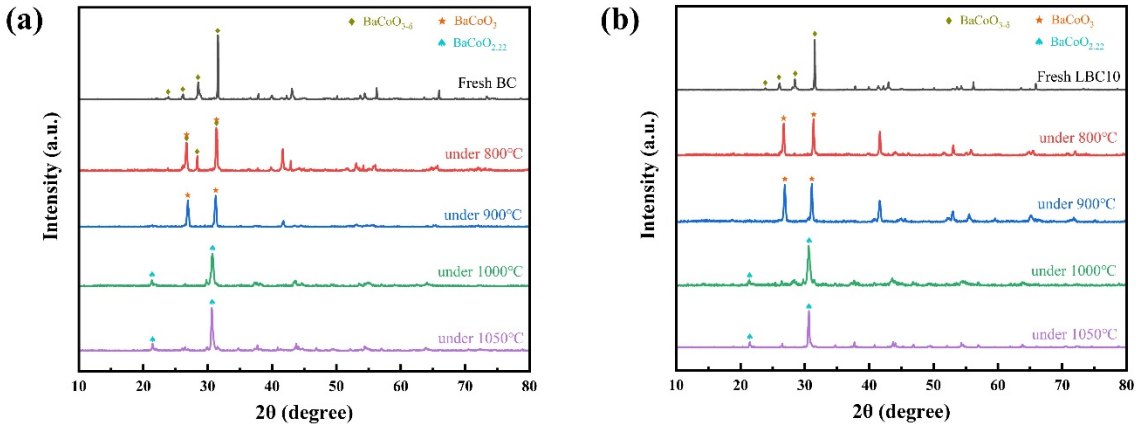

Figure S10. The crystal phase composition changes during reduction at 800-1050 °C characterized by XRD: (a) BC; (b) LBC10;

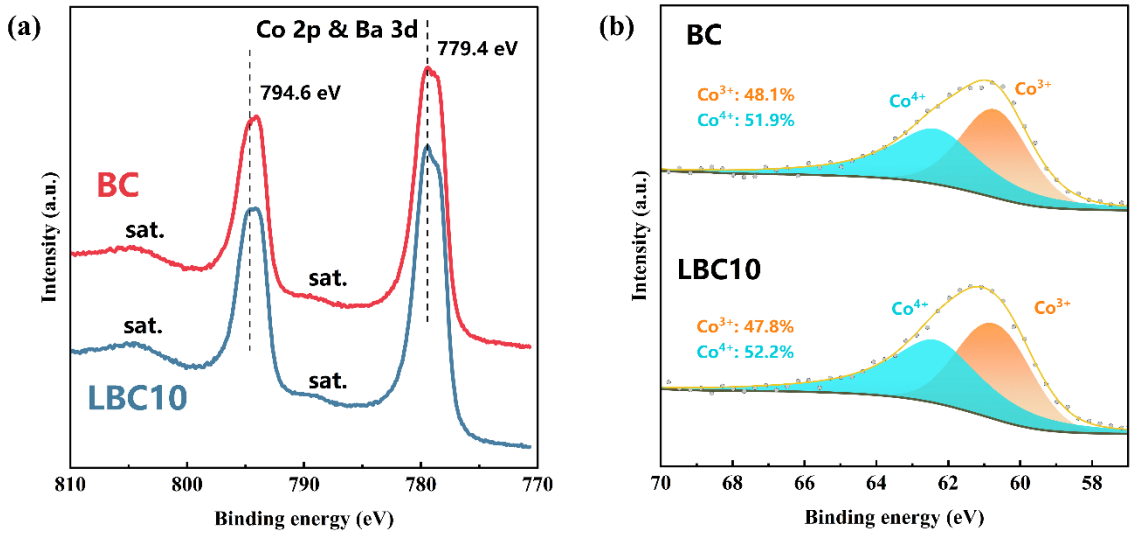

Figure S11. XPS spectra analysis: (a) Comparison of XPS Co 2p and Ba 3d spectra for raw BC and LBC10; (b) Comparison of XPS Co 3p spectra for raw BC and LBC10;

Table S2. The Li content in LBC10 and LBC15 before and after 450 cycles (via ICP, where the mass fraction refers to the proportion of Li in the total mass of metal elements within the mixed metal oxides)

Sample name	Initial mass fraction of Li	Initial stoichiometric ratio of Li	Mass fraction of Li after 450 cycles	Stoichiometric ratio of Li after 450 cycles
LBC10	0.278%	0.100	0.260%	0.088
LBC15	0.445%	0.143	0.428%	0.129

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