Supporting Information

High cathode utilization efficiency through interface engineering in all-solid-state lithium metal battery

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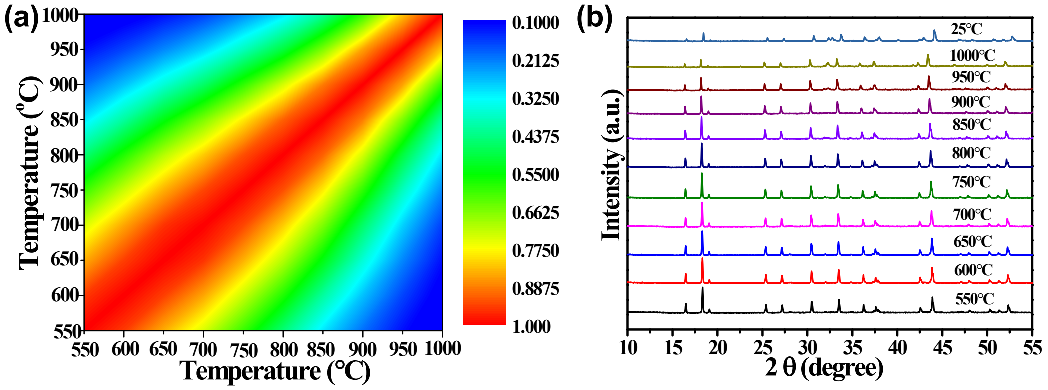

Fig. S1 **a,** Contour plot of 2D covariance analysis of HTXRD patterns. **b,** The corresponding *in-situ* XRD patterns with the appearance of new phase from 550 to 1000 °C and cooling down to 25°C.

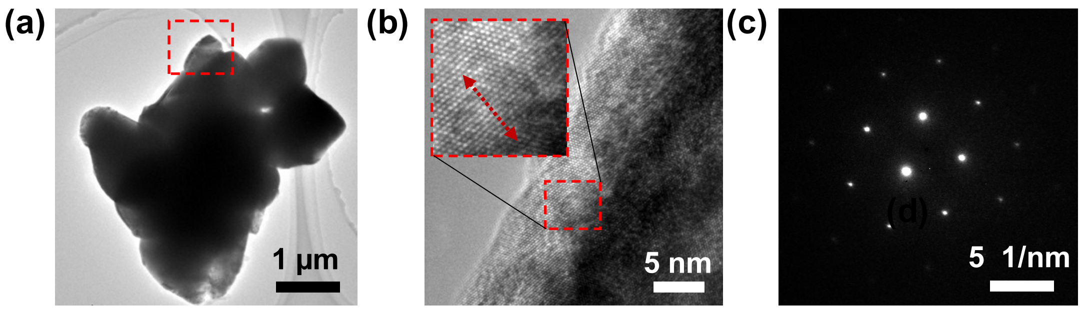

Fig. S2 **a,** The typical particle of NCM622 MCG material. **b,** The corresponding high-resolution transmission electron microscopy (HRTEM) with the d spacing of 0.242 nm and **c,** selected area electron diffraction (SAED) pattern for the (101) plane of the red marked area of **a**.

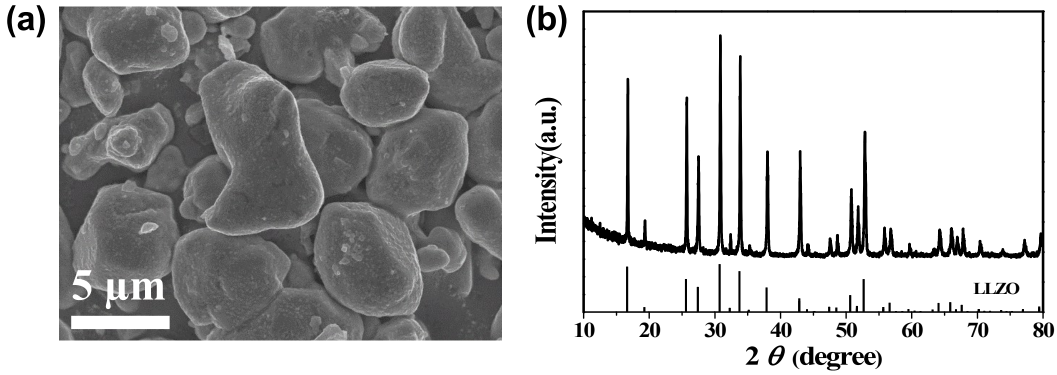

Fig. S3 a, The SEM image and **b,** XRD pattern of the commercial LLZTO powder.

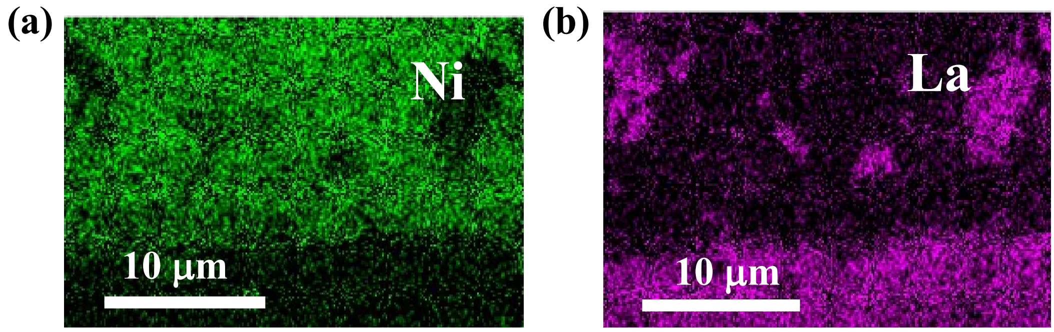

Fig. S4 The elemental mappings of La and Ni in the NCM622 MCG based composite cathode after co-sintering.

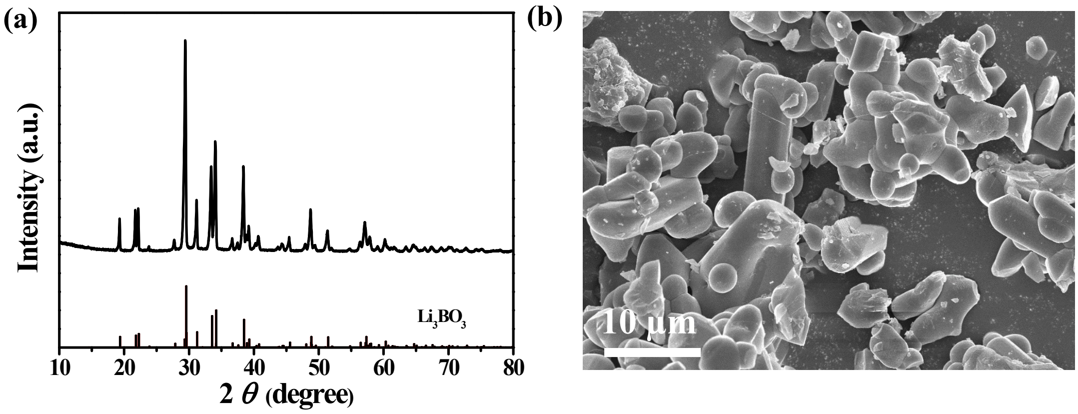

Fig. S5 a, The XRD pattern and **b,** SEM image of as-prepared LBO.

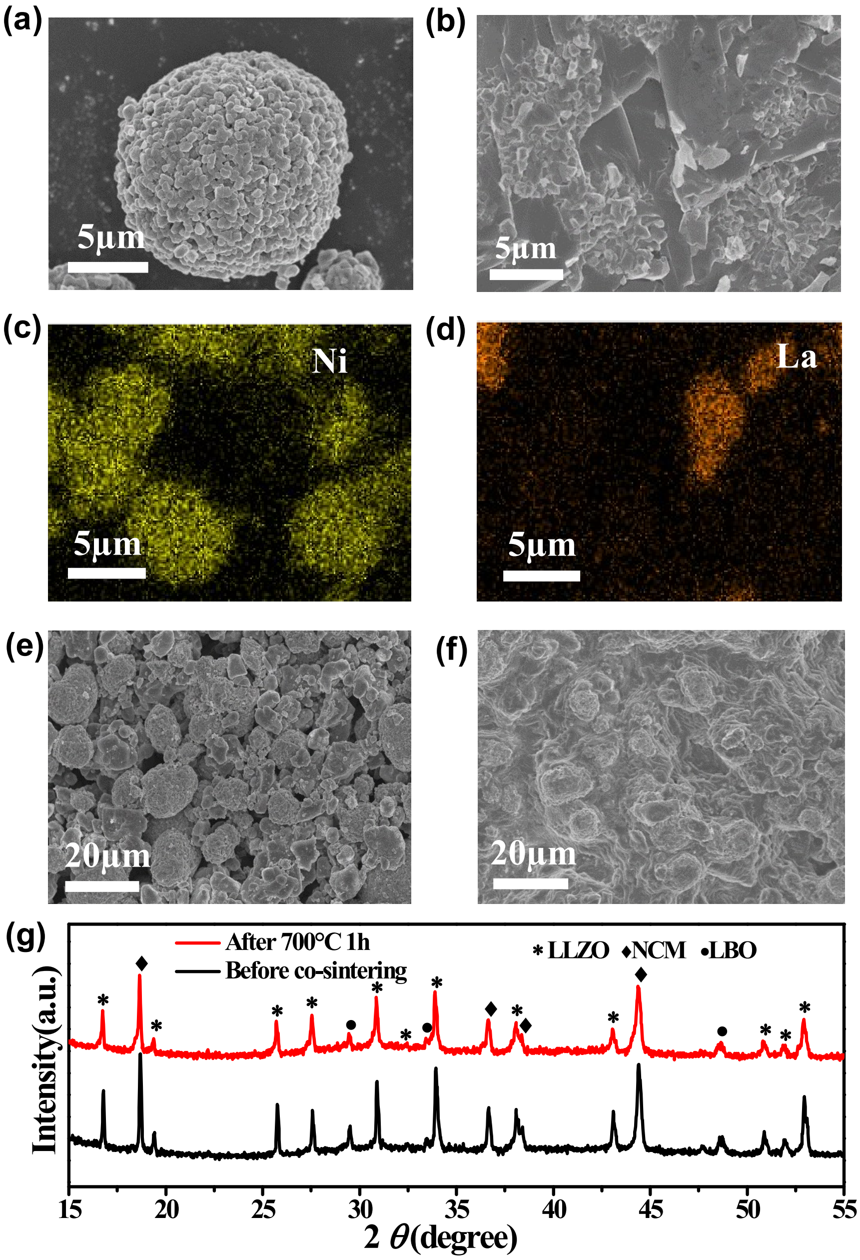

Fig. S6 a, Morphology of NCM622 spherical agglomerates. **b,** The cross-sectional SEM images of the composite cathode with agglomerates and LLZTO particles after co-sintering. **c-d,** The elemental mappings of Ni and La in the composite cathode after co-sintering. **e-f,** The SEM images of the top surface of composite cathode before (insert) and after co-sintering. **g,** The XRD patterns of composite cathode with LBO additive before and after co-sintering.

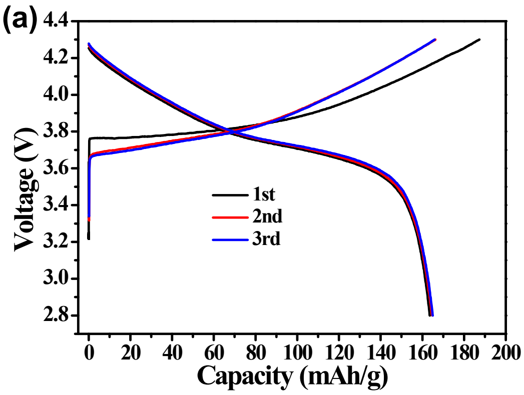

Fig. S7. The charge-discharge curves of NCM622 cathode material with **a,** MCG and **b,** agglomerates in the liquid electrolyte based batteries at the same current densities.

Table S1 The comparisons of electrochemical performces with LLZO supporting bulk-type ASSLMBs with NCM or LCO cathode material.

Configuration of the solid state battery	**Cathode**	**Temper-ature**	**Current density**	**Voltage Range (V)**	**Initial Capacity (mAh/g)**	**Cycles**	**Final Capacity (mAh/g)**	**Ref.**
NCM523+LBO+ITO/LLZTO/Li	agglomerates	80 °C	5 μA/cm²	3.0-4.6	123.3	5	76.6	[45]
NCM622+LBO+LLZTO/LLZTO/Gel/Li	agglomerates	RT	0.05 C (1C=115mA/g)	3.0-4.2	106	30	74.2	[46]
LCO+LLZTO+LCBO/LLZTO/Li	micro-sized particles	100°C	0.05 C (1C=115mA/g)	3.0-4.05	106	40	67	[47]
LCO+LBO+ITO/LLZTO/Li	micro-sized particles	80°C	5 μA/cm²	2.8-4.3	69.6	1	69.6	[59]
NCM622+LBO+LLZTO/LLZO/Li	**MCG**	**80°C**	**0.05 C (1C=180mA/g)**	**2.8-4.3**	**138.8**	**50**	**79**	**This work**

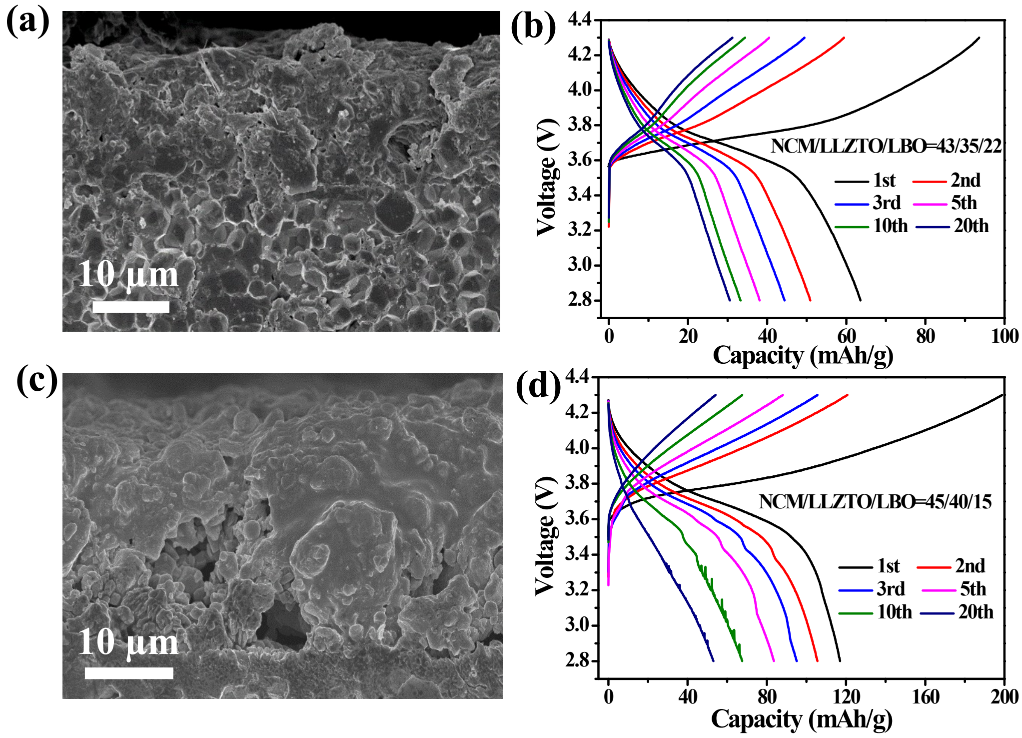

Fig. S8. a, c, The cross-sectional SEM images after co-sintering and **b,d,** the corresponding charge-discharge curves of the composite cathode by co-sintering the mixture of NCM622 MCG, LLZTO particles and LBO powder with a weight ratio of 43:35:22 and 45:40:15 at 700 ^{o}C for 1h, respectively.

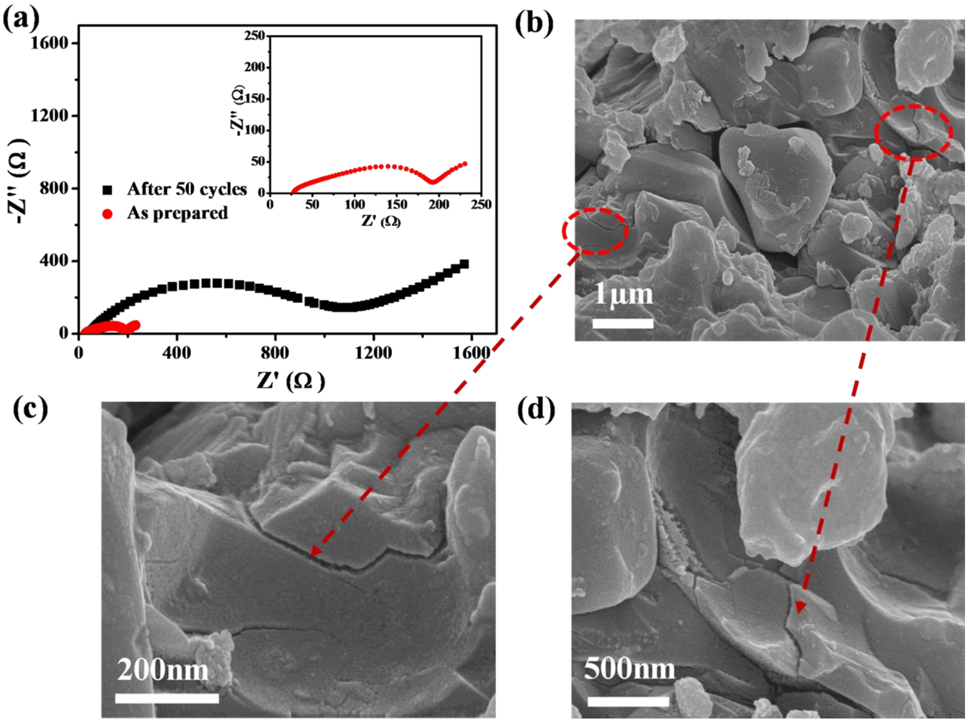

Fig. S9. a, The comparisons of EIS spectra of ASSLMBs constructed with NCM622 MCG material at the initial state and after 50 cycles. **b-d,** Cracking occurs in the composite cathode after 50 cycles.