Electric Supplementary Information

Spontaneous formation of a core–shell structure by a lithium ion conductive garnet-type oxide electrolyte for co-sintering with the cathode

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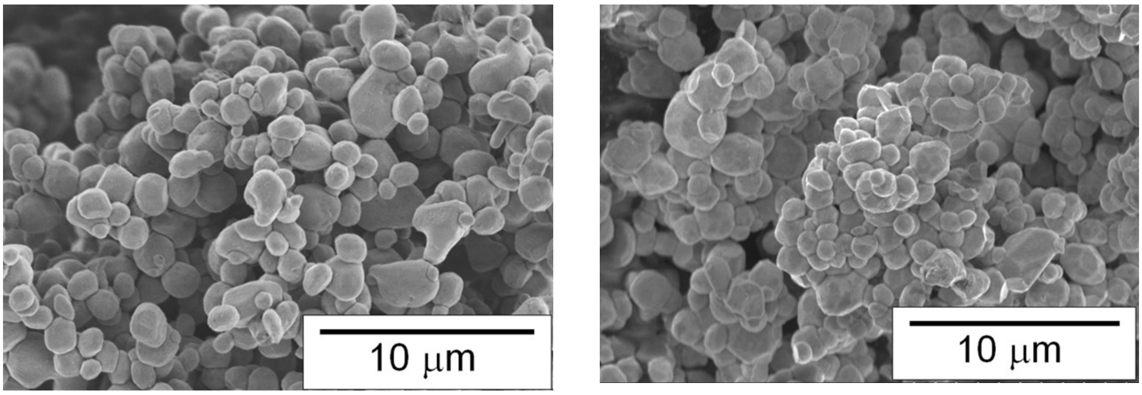

Figure S1 SEM images of Ca-LLZ (a) and Sr-LLZ (b) particles after calcination at 900 °C. The particle size of both samples was ~ 2 μm.

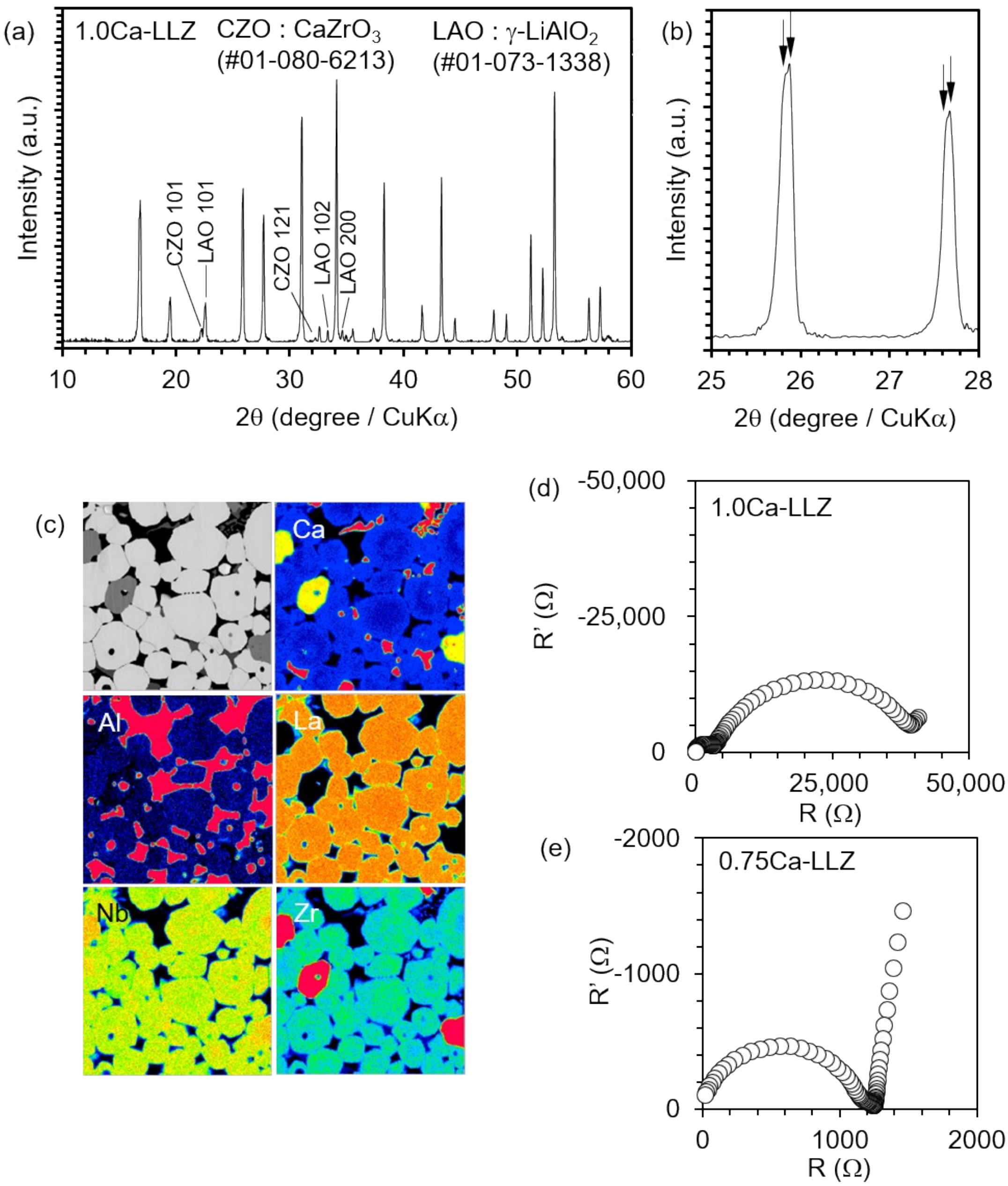

Figure S2 (a, b) XRD pattern of 1.0Ca-LLZ ($(Li_{0.64}Al_{0.2})(La_2Ca_1)(Zr_1Nb_1)O_{12})$), (c) Cross-sectional EPMA mapping images and line analysis of the elements present in 1.0Ca-LLZ, Nyquist plot for (d) 1.0Ca-LLZ and (e) 0.75Ca-LLZ.

Supplemental figure S2 shows XRD pattern (a, b), EPMA mapping images (c) and Nyqusit plot (d) for 1.0Ca-LLZ ($(Li_{0.64}Al_{0.2})(La_2Ca_1)(Zr_1Nb_1)O_{12})$) and (e) 0.75Ca-LLZ ($(Li_{0.64}Al_{0.2})(La_{2.25}Ca_{0.75})(Zr_{1.25}Nb_{0.75})O_{12})$) as comparison. In the XRD measurement result, peaks assigned to $CaZrO_3$ (PDF #01-080-6213) and $LiAlO_2$ (PDF #01-073-1338) were confirmed as impurities (a) and A split peak of LLZ was observed (c). Precipitation of Ca, Zr and Al was also confirmed by EPMA analysis. It is the key point that these precipitates observed at 1.0 Ca-LLZ were precipitated as independent particles, unlike Sr-LLZ, which condenses on the surface of LLZ particles (c). In addition, 1.0Ca-LLZ had a much higher resistance than 0.75Ca-LLZ shown in the AC-impedance results (d, e).

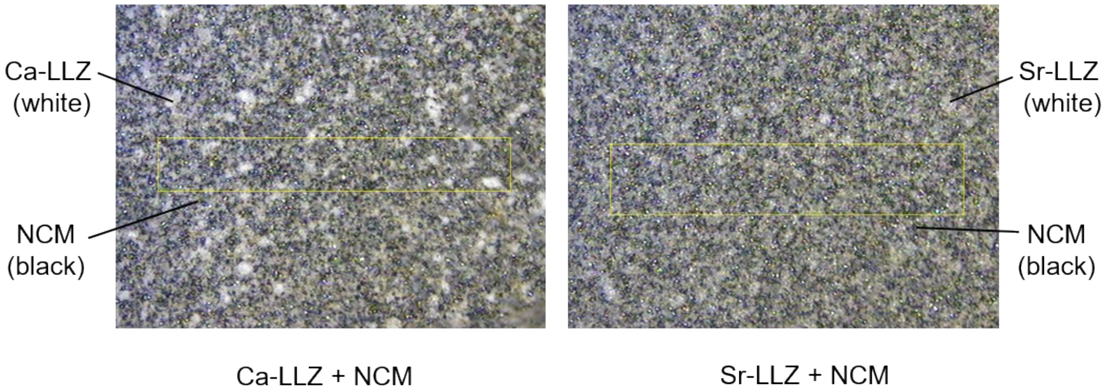

Figure S3 shows the optical micrograph images of the pellet of the mixture of NCM and Ca-LLZ (left) and Sr-LLZ (right), respectively. The mixture was die-pressed at 30 MPa into a pellet before annealing at 750 °C. The particles observed in black are NCM and the particles observed in white are LLZ.

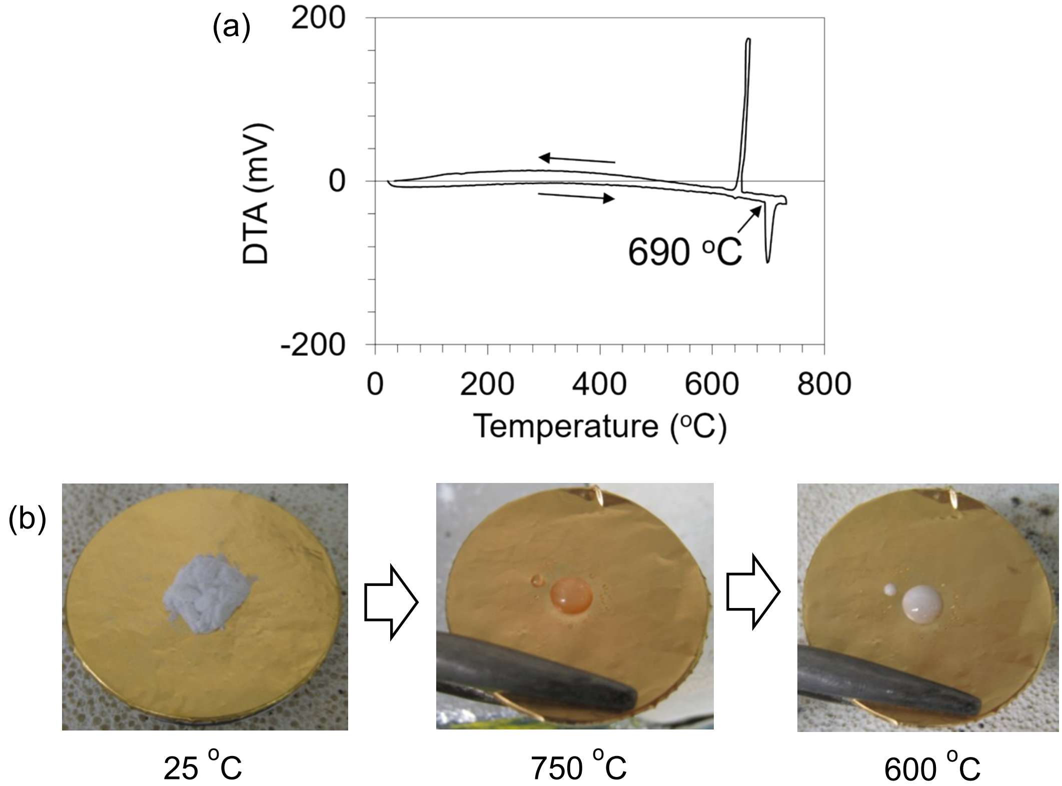

Figure S4 (a) shows DTA curve of Li_3BO_3. Heating and cooling rate are 10 ˚C / min. An endothermic reaction occurred at 690 ˚C and an exothermic reaction occurred at 650 ˚C. This result indicates that the melting temperature and solidification temperature of Li_3BO_3 are 690 ˚C and 650 ˚C, respectively.

Figure S4 (b) shows photo pictures of a morphological change of Li_3BO_3 during heating and cooling. Li_3BO_3 was heated on Au foil. These pictures were taken immediately after taking the sample from the electric furnace.

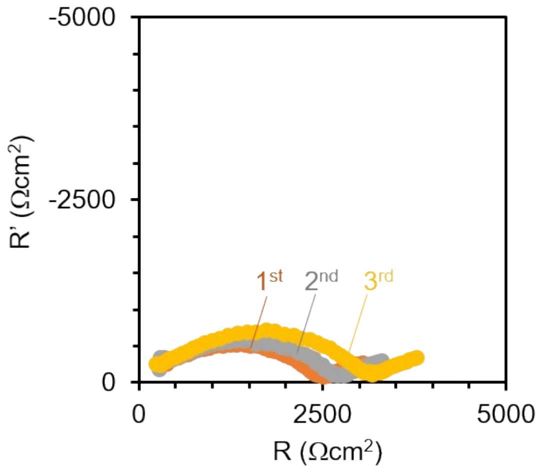

Figure S5 Nyquist plot of Li/LLZ/NCM+LLZ batteries measured at 4.6 V

The interfacial resistance of the battery was evaluated using a two-probe AC impedance method. Measurements were conducted after charging at 4.6 V vs. Li/Li^{+}. The resistance slightly increased with an increases in cylce number and the rate of increase in resistance after three cycles was ~30 %.