# A Garnet Based All Solid-State Li Battery without interface modification: Resolving of Incompatibility Issue on Positive Electrode (supplementary)

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Figure S1. Particle size distribution of composite positive electrode after 24 hours of ball milling by using yttrium stabilized zirconia balls as media and pure ethanol as solvent.

## Al-content in LLZ:Ta fabrication process

In the LLZ:Ta preparation process, a kilogram of powder was prepared at one time to ensure the LLZ:Ta has the same quality in every experiment. When preparing LLZ:Ta disks, cylindrical LLZ:Ta pellets were first made and then slice into disks with a thickness of ~ 0.6 mm, figure S2. The large amount of powder in one batch also ensures that the up taking of Al from crucible in per formula weigh is neglectable.



Figure S2. Fabricated cylindrical LLZ:Ta pellet and its sliced thin disk

During the sintering process, we found that a relative density of cylindrical pellets > 93% only available when small amount of  $Al_2O_3$  is provided in the precursors. We believe that the small amount of  $Al_2O_3$ reacts with the extra LiOH (20 mol% excess in our recipe) to form high Li contain Li-Al-O that melts around 1100 °C to serve as liquid phase sintering additive, such as  $Li_5AlO_4$  which melts at 1050 °C<sup>1</sup>, to help the densification process. Form our previous study, it takes very long dwell time, > 15 hours, at 1200 °C for Al to incorporate into LLZO to provide high Li-ion conductivity.<sup>2</sup> Therefore, it is possible for some of the Al-ions to diffuse to Li-sites in the LLZ:Ta but most of them would stay at ground boundary when the sintering time is short. Similar observation was also reported by Kotobuki *et al*.<sup>3</sup> and Kim *et al.*<sup>4</sup> Since we always need highly dense LLZ:Ta pellet to serve as solid electrolyte, it is not avoidable of using a small amount of  $Al_2O_3$  in the sintering process during our material processing. Nevertheless, it needs to be controlled at a minimum concentration so that the electrochemical performance of LCO won't be affected.

From the LCO/LLZ:Ta interface formation point of view, if all the extra 2.5 mol% of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> incorporated into LLZ:Ta, we should have a material with a formula of Li<sub>6.45</sub>Ai<sub>0.05</sub>La<sub>3</sub>Zr<sub>1.6</sub>Ta<sub>0.4</sub>O<sub>12</sub> which has much lower Al concentration than Al-substituted cubic phase LLZO. It was reported that it needs higher than 20 mol% Al to stabilize cubic phase LLZO, i.e. Li<sub>6.4</sub>Al<sub>0.2</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>, as reported by Rangasamy *et al*.<sup>5</sup> Even if all the Al-ions are diffused into LCO, the LLZ:Ta will still stay in cubic phase due to the 40 mol% Tasubstitution in Zr-sites that prevents the formation of low ionic conductive tetragonal phase LLZO at interface.



Figure S3. XRD patterns of LCO/LLZ:Ta composite positive electrode with mass ratio of 1:1 sintered at 1050 °C for 30 minutes.



Figure S4. Micro-Raman spectra and their fitting results for (a) epoxy, (b)  $LiCoO_2$ , (c)  $Li_{6.6}La_3Zr_{1.6}Ta_{0.4}O_{12}$ and (d) average spectrum from collected 6072 mapping spectra.

### Raman spectroscopy analysis

In the pristine LCO spectrum, two typical main fingerprints of Raman bands for layered rock-salt crystalline structure of high temperature LCO are at 485 and 594 cm<sup>-1</sup>, which are corresponding to the O-Co-O bending ( $E_g$ ) mode and Co-O stretching ( $A_{1g}$ ) mode, respectively.<sup>6-8</sup> The appearance of a band at 1170 cm<sup>-1</sup> was explained by Gross *et al.* that is attributes to the overtone of the  $A_{1g}$  mode due to the electronic transition in a resonance enhancement process from Co-T<sub>2g</sub> to Co-E<sub>g</sub> bands while a band at 988 cm<sup>-1</sup> is not yet clear.<sup>7</sup> Additionally, a band at 670 cm<sup>-1</sup> ( $A_{1g}$ ), figure S2(b), from Co<sub>3</sub>O<sub>4</sub> was also observed that is attributed to the characteristic of the octahedral sites (CoO<sub>6</sub>) in the  $O_h^7$  spectroscopic symmetry.<sup>9-11</sup> The Raman spectrum from pristine LLZ:Ta shows broad and overlapping bands which are able to be assigned to different vibration modes by using curve fitting, figure S2(c). The result is in agreement with Tietz *et al.* 

to be cubic phase LLZO.<sup>12</sup> One of the distinct band for LLZ:Ta is the additional band at 736 cm<sup>-1</sup> for the stretching of  $TaO_6$  octahedra other than that for  $ZrO_6$  octahedra of LLZO at 646 cm<sup>-1</sup> due to the partially substitution of Zr by Ta.<sup>13</sup>

## Synthesis of LaCoO<sub>3</sub> and Li<sub>6.3</sub>Co<sub>0.1</sub>La<sub>3</sub>Zr<sub>1.6</sub>Ta<sub>0.4</sub>O<sub>12</sub>

LaCoO<sub>3</sub> powder was prepared via a three steps solid-state reaction. The starting materials  $La_2O_3$  (Merck, 99.9%, pre-dry at 900 °C for 10 h) and CoCO<sub>3</sub> (Alfa Aesar, 99.5%) for producing 10 grams of LaCoO<sub>3</sub> were mixed in stoichiometric by using an agate mortar and pestle. The mixed powder was pressed into pellets for two sessions of calcination, once at 850 °C for 15 hours and once at 1050 °C for 10 hours with grinding and pressing in between the calcination steps. Then, the grinding and pressing were repeated before the pellets were sinter at 1200 °C for 10 hours. The sintered pellets were check by XRD for its phase purity before subjecting for micro-Raman measurements.

For Co-substituted LLZ (LLZ:Ta) , i.e. designed as  $Li_{6.3}Co_{0.1}La_3Zr_{1.6}Ta_{0.4}O_{12}$ , powder was also prepared via a three steps solid-state reaction. The starting materials LiOH·H<sub>2</sub>O (Merck, 98%), La<sub>2</sub>O<sub>3</sub> (Merck, 99.9%, predry at 900 °C for 10 h), ZrO<sub>2</sub> (Treibacher, 99.5%), CoCO<sub>3</sub> (Alfa Aesar, 99.5%) and Ta<sub>2</sub>O<sub>5</sub> (Inframat, 99.95%) for producing 10 grams of  $Li_{6.3}Co_{0.1}La_3Zr_{1.6}Ta_{0.4}O_{12}$  were mixed in stoichiometric amounts with 20 mol % LiOH·H<sub>2</sub>O in excess. The calcination and sintering procedures were the same as that for producing LaCoO<sub>3</sub>. The sintered pellets also checked by XRD for its phase purity before the micro-Raman measurements were carried out.



Figure S5. Micro-Raman spectra of LaCoO<sub>3</sub> using 1% laser power (0.25 mW) with (a) 5 second and (b) 120 second accumulative time. The inset in figure S3 (a) shows the single crystal where micro-Raman spectra were taken.

## Results of Raman spectroscopy of LaCoO<sub>3</sub> and Co-substituted LLZ:Ta

The micro-Raman spectrum for single crystal LaCoO<sub>3</sub> is shown in figure S3. The spectrum in figure 3(b) is in agreement with Ishikawa *et al.* that the Raman band could be assigned to 162 cm<sup>-1</sup> ( $E_g$ , La vibration), 231 cm<sup>-1</sup> ( $A_{1g}$ , Rotation around c), 478 cm<sup>-1</sup> ( $E_g$ , bending), 547 cm<sup>-1</sup> ( $E_g$ , quadrupole) and 645 cm<sup>-1</sup> ( $A_{2g}$ , breathing) at RT for which Raman band at 162 cm<sup>-1</sup> and 654 cm<sup>-1</sup> are pronounced with low accumulative time of the spectrum.<sup>14</sup> When compared the Raman spectrum to that from Zhu et al. (referenced by Ren et al.<sup>15</sup>), the Raman spectrum in Zhu's report has much higher noise-signal ratio that could be a result from low spectrum accumulative time when doing the Raman measurement.<sup>16</sup> Three broad peaks in the spectra were label to 138, 305 and 675 cm<sup>-1</sup> without fitting. The peak at 675 cm<sup>-1</sup> was assigned as second-order Raman scattering of LaCoO<sub>3</sub> by Ren *et al.* that was referenced to Podobedov *et al.* as a result from Raman spectroscpoy investigation of LaMnO<sub>3</sub>.<sup>17</sup> No detail about how the Raman measurements were done in their experimental section that make it difficult to judge the Raman results. In either case, the Raman band at 685 cm<sup>-1</sup> in Ren's report cannot origin from LaCoO<sub>3</sub> due to its strong intensity and much higher wavenumber. Therefore, a Co-substituted LLZ:Ta was synthesized for clarify the origin of this strong peak at 685 cm<sup>-1</sup>.

The micro-Raman spectrum which was taken from a single crystal of synthesized Co-substituted LLZ:Ta shows an identical pattern as that for LLZ:Ta, except an extra peak at 693 cm<sup>-1</sup>, figure S4. Since the highenergy region above 550 cm<sup>-1</sup> shows the vibrational stretching modes of octahedral units, the assignment of this peak at 693 cm<sup>-1</sup> was first considered as a result of substituted Co sitting on octahedral sites as that for TaO<sub>6</sub> and ZrO<sub>6</sub>.<sup>12</sup> However, the bond strength of Co-O (384.5 ± 13.4 kJ mol<sup>-1</sup>) is much lower than that for Zr-O (776.1 ± 13.4 kJ mol<sup>-1</sup>) and Ta-O (799 ± 12.6 kJ mol<sup>-1</sup>) which makes the vibrational stretching mode of CoO<sub>6</sub> octahedral units must appear at the lower wavenumber than that for ZrO<sub>6</sub>.<sup>18</sup> Furthermore, the aliovalent substitutions such as Al<sup>3+</sup>, Ga<sup>3+</sup> and Fe<sup>3+</sup> in garnet structured LLZO usually favor tetrahedral sites than octahedral ones.<sup>19-22</sup> The two reasons make the assignment of the Raman band at 693 cm<sup>-1</sup> as the vibrational stretching mode of CoO<sub>6</sub> octahedral units suspicious. Therefore, different excitation wavelengths were used for micro-Raman investigation of Co-substitution LLZ:Ta, figure S5. When using excitation wavelength of 457 nm, it was observed that the intensity of peak at 693 cm<sup>-1</sup> is much higher than that for  $ZrO_6$  (646 cm<sup>-1</sup>) and  $TaO_6$  (737 cm<sup>-1</sup>) and three photoluminescence peaks are detected at 1380 cm<sup>-1</sup>, 2063 cm<sup>-1</sup> and 2737 cm<sup>-1,23</sup> It is noticed that the photoluminescence peaks have a wavenumber difference in between the peaks of about 680 cm<sup>-1</sup> which make it possible that the peak at 693 cm<sup>-1</sup> is the first photoluminescence peak due to the Co-substituent in LLZ:Ta. To further confirm the result, another excitation wavelength of 785 nm was used for the micro-Raman study. It can be seen that the intensity of peak at 693 cm<sup>-1</sup> is much lower than that for  $ZrO_6$  (646 cm<sup>-1</sup>) and  $TaO_6$  (737 cm<sup>-1</sup>). No photoluminescence peak was observed at high wavenumber region when using excitation wavelength of

785 nm. It is, therefore, confirm the peak at 693  $\text{cm}^{-1}$  is a photoluminescence peak due to the Co-substituent in LLZ:Ta.<sup>23</sup>



Figure S6. Micro-Raman spectrum of  $Li_{6.3}Co_{0.1}La_3Zr_{1.6}Ta_{0.4}O_{12}$ . The inset in figure S4 shows the single crystal where micro-Raman spectrum was taken.



Figure S7. Micro-Raman spectrum of  $Li_{6.3}Co_{0.1}La_3Zr_{1.6}Ta_{0.4}O_{12}$  by using different excitation wavelength. It is confirmed that the peak at 693 cm<sup>-1</sup> is a photoluminescence peak due to the substitution of Co in LLZ:Ta.



Figure S8. Micro-Raman spectra and their fitting results at different points of SSLB.



Figure S9. Discharge curves for long term galvanostatic cycling.





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