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Figure S1. SEM images of (a) LLOs, (b) LLOs@CNTs 1 wt%, (c) LLOs@CNTs 2 wt%, (d) LLOs@CNTs 4 wt%.

SEM images of LLOs@CNTs composites with different CNTs contents are displayed in Figure S2. The pristine LLOs are a smooth nano-micron spheroid (Figure S1a). The composite with 1 wt% CNTs is coated by a few CNTs (Figure S1b). Moderate CNTs uniformly distribute on the surface of the secondary particles LLOs in the composites with 2 wt% CNTs (Figure S1c). As the content of CNTs continues to increase, superabundant CNTs aggregate on the surface of LLOs in the composite with 4 wt% CNTs, which may hinder the diffusion of Li⁺ (Figure S1d).



Figure S2. (a) Rate capabilities, Cycling performances at (b) 0.2 C and (c) 1 C of

LLOs@CNTs composites with different CNTs contents.

Figure S2a shows the rate capabilities of LLOs@CNTs composites with different CNTs contents. The three samples with CNTs exhibit better rate capability than the uncoated LLOs. The three samples with CNTs deliver lower capacity than LLOs at smaller current density (0.1 C), which may be because CNTs can impede the Li⁺ migration to some extent at small current density. The influence is more obvious at lower rate, and the sample with 2 wt% CNTs has the weakest influence to display higher capacity than two others at 0.1 C, however, the capacity of the sample with 4 wt% CNTs is slightly higher at higher rate because more CNTs increase the electronic conductivity

to a greater extent.

The cycling performances at 0.2 C of LLOs@CNTs composites with different CNTs contents are exhibited in Figure S2b. The discharge capacity of pristine LLOs suffers from a rapid decrease from 193.2 to 108.6 mA h g⁻¹ with a capacity retention rate of 56.2% after 100 cycles. By comparison, the sample with 2 wt% CNTs delivers the highest and the most stable discharge capacity due to moderate CNTs with one-dimensional channel enhancing the electronic conductivity and ionic conductivity simultaneously. Its discharge capacity after 2 cycles and after 100 cycles at 0.2 C is 213.3 and 184.1 mA h g⁻¹, respectively (capacity retention rate of 86.3%).

Figure S2c displays the cycling performances at 1 C of LLOs@CNTs composites with different CNTs contents. The sample with 4 wt% CNTs delivers the highest discharge capacity (160.3 mA h g⁻¹ after 2 cycles), but the sample with 2 wt% CNTs presents the most stable cycling performance during 500 cycles (capacity retention rate of 85.2%). By contrast, the discharge capacity of LLOs rapidly reduces from 134.4 to 48 mA h g⁻¹ after 500 cycles (capacity retention rate of 35.7%).

In conclusion, LLOs@CNTs composites with 2 wt% CNTs possess the optimal comprehensive electrochemical properties. Hence, 2 wt% CNTs were employed to prepare LLOs@LATP@CNTs composites.



Figure S3. XRD pattern of as-prepared LATP solid electrolyte.



Figure S4. TG curve of LLOs@LATP precursor.

TG curve of LLOs@LATP precursor is observed in Figure S4. A weight loss of 0.67% is observed below 100 °C due to the loss of absorbed water in the sample. In the temperature range from 100 to 412.5 °C, there is a conspicuous weight loss of 10.14% attributed to the decomposition of glycol citrate polymer. Further, a weight loss of 1.02% from 412.5 to 650 °C represents the formation of LLOs@LATP composites and the improvement of its crystallinity. When the temperature rises above 650 °C, there is still a slight loss of weight, which corresponds to Li loss at high temperature. Therefore, 650 °C is selected as the calcination temperature for the synthesis of LLOs@LATP composites.



Figure S5. The cycling performance at 1 C of all samples. The inset is the magnification figure from 200th to 500th cycle.