## **Supporting Information**

## Multi-Functional Surface Engineering for Li-excess Layered Cathode Material Targeting Excellent Electrochemical and Thermal Safety Properties

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Figure S1. FESEM images of the (a) LLMO and (b) LLMO@Li<sub>4</sub> $M_5O_{12}$ @BiOF samples.



**Figure S2.** Ni, Co, Mn, Bi and F elmental mappings of the LLMO@Li<sub>4</sub>M<sub>5</sub>O<sub>12</sub>@BiOF sample.



Figure S3. Raman patterns of the LLMO and LLMO@Li<sub>4</sub>M<sub>5</sub>O<sub>12</sub>@BiOF samples.



Figure S4. dQ/dV profiles of the LLMO and LLMO@Li<sub>4</sub> $M_5O_{12}$ @BiOF samples during the first discharge.



Figure S5. Specific energies of the LLMO and LLMO@Li<sub>4</sub> $M_5O_{12}$ @BiOF samples at the 0.2 C rate.



Figure S6. FTIR patterns of the LLMO and LLMO@ $Li_4M_5O_{12}$ @BiOF materials after three cyclces.



**Figure S7.** (a) GITT curves of the LLMO and LLMO@Li<sub>4</sub>M<sub>5</sub>O<sub>12</sub>@LBO samples during the first discharge; (b) a typical *E vs.*  $\tau^{1/2}$  profile of the samples for a single titration.

If the *E* vs.  $\tau^{1/2}$  relationship shows a linear behavior over the entire time period of current flux, the lithium diffusion coefficients (*D*<sub>*Li*</sub>) of the samples can be calculated by the following equation, <sup>[1]</sup>

$$D_{Li^{+}} = \frac{4}{\pi\tau} \left(\frac{mV_{M}}{MA}\right)^{2} \left(\frac{\Delta E_{s}}{\Delta E_{\tau}}\right)^{2}$$

where M and m are the molecular weight and mass of the cathode material, respectively.  $V_m$  is the molar volume of the active material, F is the Faraday constant and A is the BET surface area of the materials.

## References

[1] Rui, X. H.; Ding, N.; Liu, J.; Li, C.; Chen, C. H., Analysis of the Chemical Diffusion Coefficient of Lithium Ions in Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> Cathode Material. *Electrochim. Acta* 2010, 55, 2384-2390.