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Electronic Supplementary Information (ESI)

Layered Perovskite $LiEuTiO_4$ as a 0.8 V lithium intercaltion electrode

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Experimental Section

Synthesis of $LiEuTiO_4$:

$LiEuTiO_4$ was synthesized by a sol-gel method and ion-exchange reaction. First, a stoichiometric amount of Eu_2O_3 (0.003 mol, 99.99%) and Na_2CO_3 (0.0039 mol, analytical reagent, A. R. excess 30% as flux) were dissolved in dilute HNO_3 (10 mL, 2 mol/L) solution under continuous stirring, followed by removing the excess HNO_3 at high temperature (80 °C). Then, adding in appropriate amount of deionized water (10 mL) to the above mixture with fully stirring to obtain the transparent solution A. The transparent solution B was formed by mixing the calculated volumes of acetic acid (A. R. as solvent, 10 mL), ethanol (A. R. as hydrolysis inhibitors, 10 mL) and 0.006 mol tetrabutyl titanate ($Ti(OC_4H_9)_4$) under stirring. Subsequently, adding solution B dropwise into solution A under continuous stirring to get the final transparent solution. Then, the final solution was dried at 70 °C for 24 h followed by dried at 120 °C for 24 h in an oven to form a white dried gel. Next, the dried gel was grinded in a mortar and preheated at 500 °C for 2 h, and then sintered at 900 °C for 7 h in a furnace to obtain $NaEuTiO_4$. Ion-exchange was conducted between the Na ions in $NaEuTiO_4$ and Li ions in molten $LiNO_3$ (0.0078 mol). Finally, the products were washed with deionized water and air-dried (70 °C for 12 h) to get the required samples $LiEuTiO_4$.

Material characterization:

Powder X-ray diffraction (XRD) measurements were performed using BRUKER D8 ADVANCE with Cu-Kα radiation. Samples with different state of discharge/charge for X-ray diffraction were made electrochemically. After discharge/charge, cells were opened in an argon-filled glove box. Then, The electrodes were washed with dimethyl carbonate to remove residual electrolyte and left under vacuum until all solvent had evaporated before measurements. X-ray photoelectron spectroscopy (XPS) experiments were conducted on an K-Alpha+ (Thermo Scientific) instrument with monochromatic Al Kα X-ray radiation (1486.6 eV, 400μm). Field-emission scanning electron microscopy (FE-SEM) studies were carried out using a Nova NanoSEM 450 (FEI Company) instrument.

Electrochemical characterization:

The working composite electrodes were fabricated with the active material $LiEuTiO_4$, super P carbon and sodium carboxymethyl cellulose (CMC) binder in a mass ratio of 70:20:10. The mixture was then coated on copper foil using deionized water as the solvent, followed by drying at 110 °C for 12 h in vacuum oven. Electrochemical half-cells consisted of a $LiEuTiO_4$ composite electrode, a lithium sheet-metal counter electrode and monolayer polyethylene separator saturated with electrolyte of a 1 M $LiPF_6$ solution in ethylene carbonate-dimethyl carbonate (1:1, v/v). Electrochemical measurements were conducted using CR 2016 button type lithium battery assembled in an argon-filled MBRAUN Unilab glovebox ($H_2O/O_2 < 1$ ppm). Galvanostatic charge/discharge tests were measured on LAND CT2001A battery test system from 0.01 to 3.0 V at 25 °C. Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS) were implemented on a CHI660D (CH Instruments Ins.) electrochemical workstation.

Fig. S1.

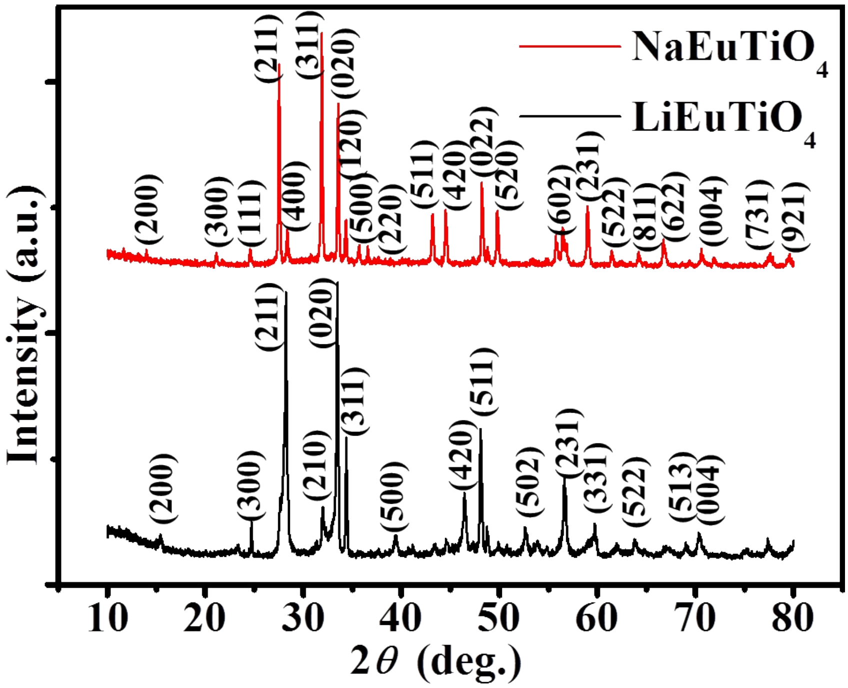

Fig. S1. Powder X-ray diffraction patterns of NaEuTiO4 and LiEuTiO4.

The XRD patterns peaks of NaEuTiO$_4$ are indexed and identified according to the standard PDF Card #47-0004. The XRD patterns peaks of LiEuTiO$_4$ are indexed according to the reported literature[1, 2].

Fig. S2.

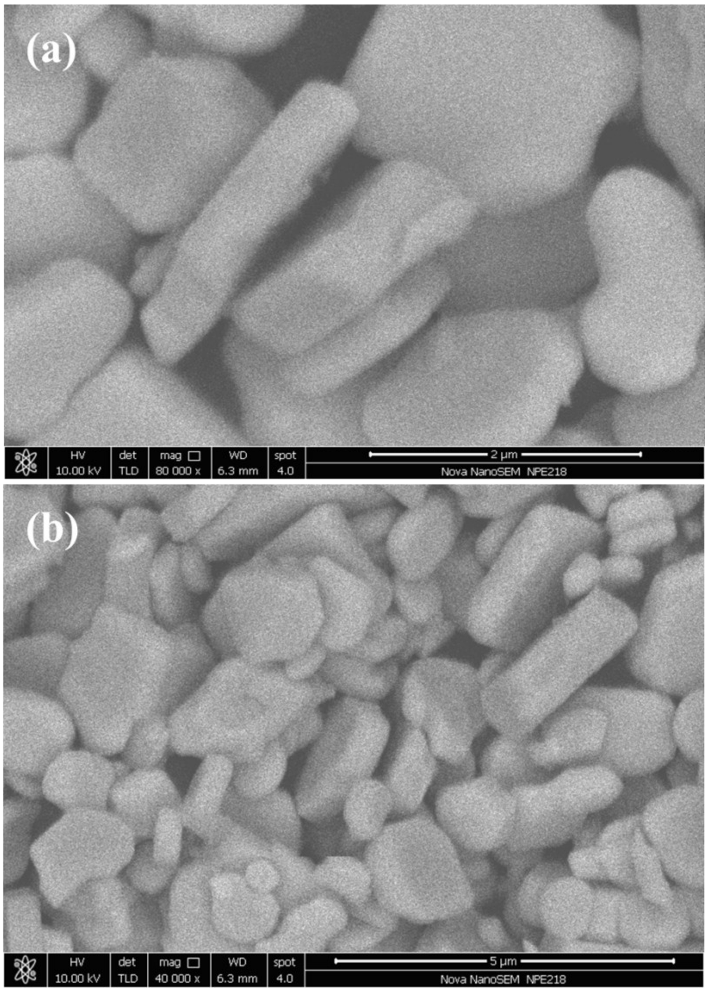

Fig. S2. SEM images of $LiEuTiO_4$ sample.

Fig. S3.

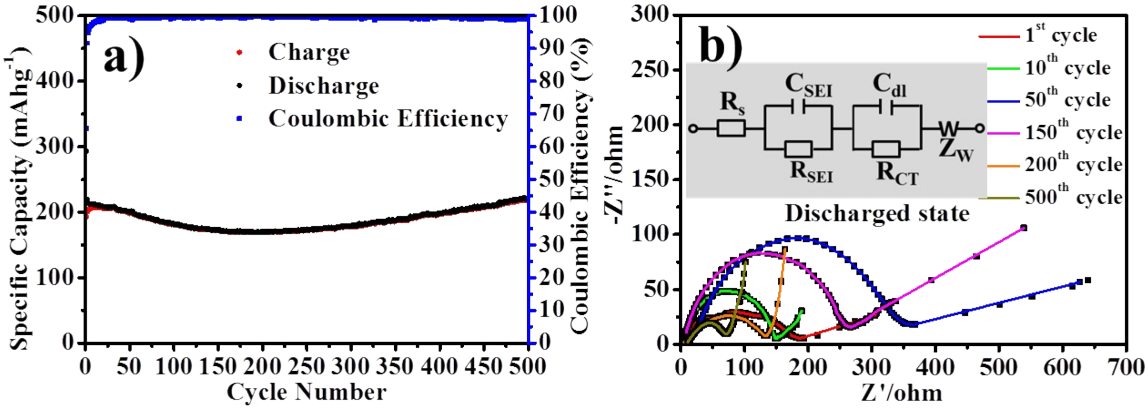

Fig. S3. (a) Cycling performances and coulombic efficiency at 100 mAg^{-1}. (b) A.C. impedance spectra collected at the end of the 1st, 10th, 50th, 150th, 200th, 500th cycle (Line for fitting, point for experiment).

Generally, in impedance spectra, the intercept of the curve with the X-axis in the high frequency range is related to the intrinsic resistance of the cell (R_S), the two overlapped semicircles in the high-medium frequency range correspond to the solid electrolyte interphase film resistance (R_{SEI}) and the charge transfer resistance (R_{CT}), and the linear region in the low frequency range is associated with the Warburg resistance (Z_W). In the fitted equivalent circuit, shown in the inset, the corresponding impedance values are shown in Table S1.

Fig. S4.

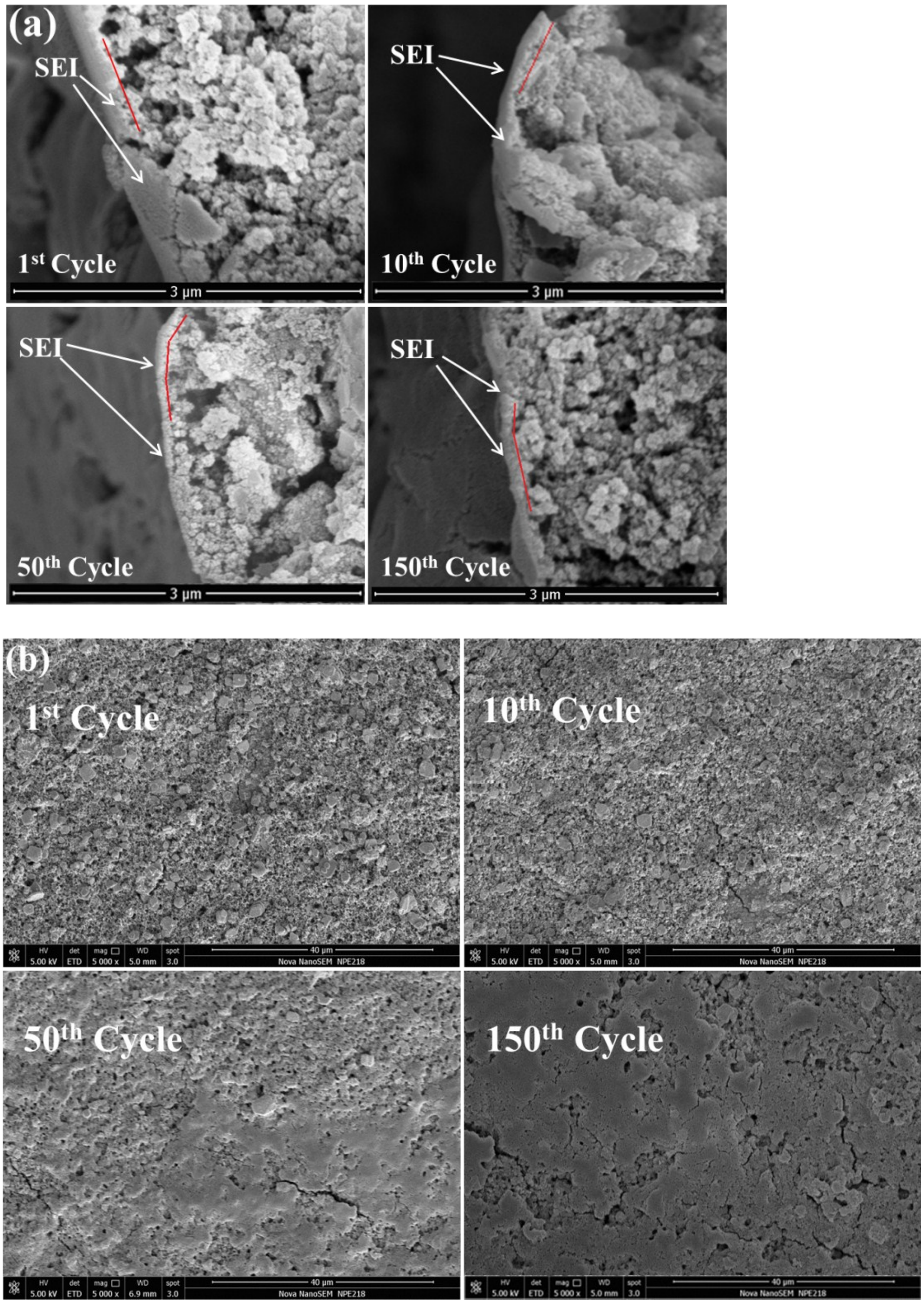

Fig. S4. SEM images of the $LiEuTiO_4$ electrodes after 1st, 10th, 50th, 150th cycles: (a) Cross-sectional, (b) Positive-sectional.

Fig. S5.

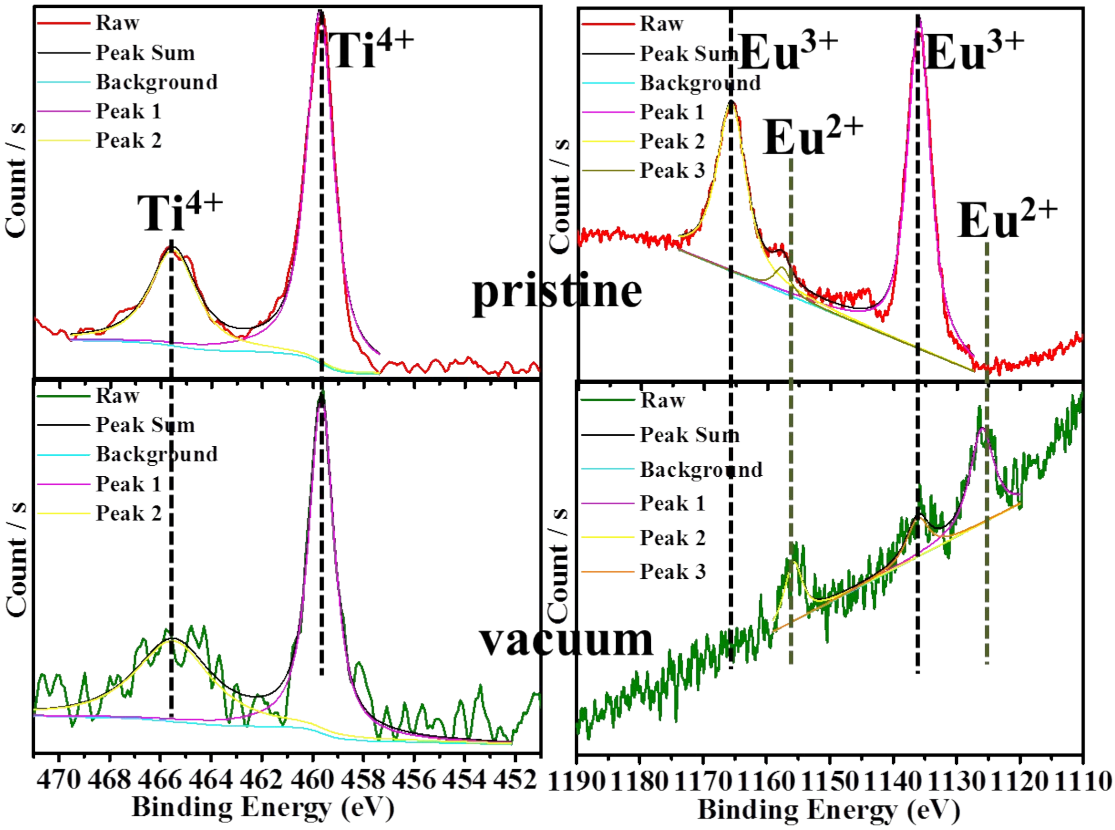

Fig. S5. The XPS peak differentation-imitaing analysis (Samples: Pristine and After 1st discharge to 0.01 V (XPS in vacuum)).

Table S1. Fitting data of the resistance of the $LiEuTiO_4$ electrodes with the equivalent circuit. (After 1st, 10th, 50th, 150th, 200th, 500th cycles)

Cycle	R_S	R_{SEI}	R_{CT}
1st /Ω	6.103	24.87	153.1
10th /Ω	4.178	57.85	82.01
50th /Ω	16.82	162.4	186.2
150th /Ω	4.786	86.27	161
200th /Ω	5.02	41.72	93.54
500th /Ω	5.57	16.79	54..8

References

1. T. Kenji, K. Satoru and S. Mineo, *J. Ceram. Soc. Jpn.*, 1996, **104**, 140-142..
2. S.-H. Song, K. Ahn, M. G. Kanatzidis, J. A. Alonso, J.-G. Cheng and J. B. Goodenough, *Chem. Mater.*, 2013, **25**, 3852-3857.