Layered Perovskite LiEuTiO$_4$ as a 0.8 V lithium intercalation 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$_2$O$_3$ (0.003 mol, 99.99%) and Na$_2$CO$_3$ (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$_4$H$_9$)$_4$) 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-K$\alpha$ 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 K$\alpha$ 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 LiEuTiO₄ composite electrode, a lithium sheet-metal counter electrode and monolayer polyethylene separator saturated with electrolyte of a 1 M LiPF₆ 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 (H₂O/O₂ < 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. Powder X-ray diffraction patterns of NaEuTiO$_4$ and LiEuTiO$_4$.

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. SEM images of LiEuTiO$_4$ sample.
Fig. S3. (a) Cycling performances and coulombic efficiency at 100 mAg$^{-1}$. (b) A.C. impedance spectra collected at the end of the 1$^{st}$, 10$^{th}$, 50$^{th}$, 150$^{th}$, 200$^{th}$, 500$^{th}$ 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. SEM images of the LiEuTiO$_4$ electrodes after 1st, 10th, 50th, 150th cycles: (a) Cross-sectional, (b) Positive-sectional.
Fig. S5. The XPS peak differentiation-imitating 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 1$^{st}$, 10$^{th}$, 50$^{th}$, 150$^{th}$, 200$^{th}$, 500$^{th}$ cycles)

<table>
<thead>
<tr>
<th>Cycle</th>
<th>$R_S$ (Ω)</th>
<th>$R_{SEI}$ (Ω)</th>
<th>$R_{CT}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^{st}$/Ω</td>
<td>6.103</td>
<td>24.87</td>
<td>153.1</td>
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<tr>
<td>10$^{th}$/Ω</td>
<td>4.178</td>
<td>57.85</td>
<td>82.01</td>
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<td>50$^{th}$/Ω</td>
<td>16.82</td>
<td>162.4</td>
<td>186.2</td>
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<tr>
<td>150$^{th}$/Ω</td>
<td>4.786</td>
<td>86.27</td>
<td>161</td>
</tr>
<tr>
<td>200$^{th}$/Ω</td>
<td>5.02</td>
<td>41.72</td>
<td>93.54</td>
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<tr>
<td>500$^{th}$/Ω</td>
<td>5.57</td>
<td>16.79</td>
<td>54.8</td>
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References