

## **Electronic Supplementary Information**

### **A polyimide ion-conductive protection layer to suppress side reactions on $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode at elevated temperature**

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## **Experimental section**

### **Materials**

Pyromellitic dianhydride (PMDA, purity: 99%), oxydianiline (ODA, purity: 98%) and N, N-Dimethylacetamide (DMAc, purity: 99.8%) were purchased from Aladdin. The DMAc was dried with 4Å molecular sieves prior use. The LTO (average particle size: 1 μm) was purchased from Tianjiao Technology, Shenzhen, China. The electrolyte was 1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume, Shenzhen Capchem Technology Co., Ltd.).

### **Synthesis of polyamic acid**

Synthesis of the polyamic acid has been described in details in previous study<sup>26</sup>. The polyamic acid was synthesized via the polycondensation of PMDA and ODA with an equivalent molar ratio. ODA (0.957 g, 4.78 mmol) was completely dissolved in 18 g of DMAc with stirring in a three-neck flask at room temperature. PDMA (1.043 g, 4.78 mmol) was added into the ODA solution in four aliquots in 1 h. Then, the stirring of the above mixture was continued for 8 h. The solid content of the pristine polyamic acid solution was 10%. All the above steps were performed in argon atmosphere. The resulting polyamic acid solution was kept in a refrigerator for the next step.

### **Preparation of polyimide-coated LTO**

The concentration of the polyamic acid coating solution was diluted to 2.5 wt% by DMAc. LTO powders were added to the polyamic acid coating solution, which was then stirred for 60 min and subsequently centrifuged (7000 rpm, 10 min). The centrifuged powders were dried at ambient temperature for 1 h and further vacuum-dried at the same temperature for 24 h. The thickness of polyimide coating is

controlled by varying polyamic acid (a precursor polymer of the polyimide) concentration of coating solutions. Meanwhile, in order to convert the polyamic acid into polyimide, the polyamic acid-wrapped LTO powders were thermally imidized via a stepwise imidization process (80 °C for 2 h /150°C for 1 h /200°C for 1 h /250°C for 1 h /300°C for 1 h) under an argon atmosphere.

### **Sample analysis**

The surface morphology of the polyimide-wrapped LTO was examined using a transmission electron microscope (TEM, JEM-2010, JEOL) with an energy-dispersive spectrometer (EDS). The imidization reaction of the polyamic acid was confirmed using a FT-IR spectrometer (Spectrum 100, Perkin Elmer, Inc., USA). The interfacial exothermic reactions between the charged LTO and the liquid electrolyte were examined by differential scanning calorimetry (DSC, TA Instruments Q2000) measurements. For DSC analysis, the LTO/Li and polyimide-LTO/Li half-cells were cycled for 5 times in a voltage range of 0.8–3.0 V at 55°C, and charged until ca. 70% lithiation state at the sixth cycle. Then the cells were stored in thermal chambers at open-circuit voltage and 55°C for five days. After storage, the cells were disassembled in a glove box to remove the charged electrodes. Approximately 5 mg of the electrode material containing liquid electrolyte was sealed in a high-pressure DSC liquid crucible. The DSC measurements were performed in a temperature range from room temperature to 350 °C at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

### **Electrochemical Measurements**

LTO anodes were fabricated by coating NMP-based slurry with a mixture of 80 wt% of LTO, 10 wt% of polyvinylidene fluoride (PVdF) binder and 10 wt% of carbon

black on copper foil. A unit cell (2016-type coin) was assembled by sandwiching a PE separator (thickness = 20  $\mu\text{m}$ , ENTEK) between a lithium metal and the LTO anode. The cycling performances of coin cells were measured on a Land CT2001 battery test system at 55°C. The LTO/Li and polyimide-coated LTO/Li half-cells were cycled for 5 times in a voltage range of 0.8–3.0 V at 55°C, and then charged until ca. 70% lithiation state at the sixth cycle. Subsequently the cells were stored in thermal chambers at open-circuit voltage and 55°C for five days. After storage, the cells continued on cycle at 55°C. Electrochemical impedance spectroscopy (EIS) was measured using a frequency response analyzer (CHI660C) with an electrochemical interface in the frequency range from 100 KHz to 0.01 Hz at 55°C. A supplementary experiment for evaluating the ionic conductivity of a polyimide film swelled with the liquid electrolyte (1 M  $\text{LiPF}_6$  in EC/DMC = 1/1, v/v) was carried out. The ionic conductivity was measured by ac impedance spectroscopy using a CHI660C electrochemical analyzer in the frequency range from 100 KHz to 1 Hz at room temperature.