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Electronic Supplementary Information

Fluoride scavengeable Sb_2O_3-functionalized poly(imide) separators for prolonged cycling of lithium-ion batteries

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1. Experimental

1.1 Sample preparation

To prepare the Sb_2O_3 slurry, 0.0325 g of PVdF-HFP binder was dissolved in NMP to form the binder solution. Then, 0.163 g of Sb_2O_3 was dispersed in the binder solution for one hour. Subsequently, the coating slurry was cast onto the PI separators using a doctor blade. The loading of the material was controlled according to the doctor blade. The loading of the Sb_2O_3 coating layer was fixed at 0.85 mg cm^{-2}. The modified PI-based separators with Sb_2O_3 were used without additional treatment.

1.2 Materials characterization

The surface morphology of the PI-based separator was analyzed using scanning electron microscopy (SEM). Mechanical properties were measured using a tensile testing machine with material samples measuring 1.5 cm × 5.0 cm. The characteristics of the PI-based separators with varying porosity were measured using a Gurley densometer. Electrolyte absorption rate was calculated by dividing the difference in weight of the PI-based separator before and after immersion in the electrolyte by the weight before immersion in the electrolyte. In addition, 0.1 mL electrolyte was dropped on the separator to compare the degree of absorption after 1 minute, and the angle of the electrolyte was confirmed through the contact angle. To compare the thermal contraction of separators as temperature increases, PE- and PI-based separators were stored at room temperature at 80, 135, 150, 180, and 200 ^oC for 30 minutes and then naturally cooled to compare thermal contraction rates. To observe the endothermic behavior of the Sb_2O_3 precursor through its reaction with halogen elements, 2 mg Sb_2O_3 and 2 μL electrolyte were added and analyzed using differential scanning calorimetry (DSC). This was carried out in N_2 atmosphere from room

temperature to 300 °C at 10 °C min^{-1}. Additionally, DSC was used to observe the O_2 release behavior occurring from the cathode when the temperature increased. After charging the NCM/Li cell once at 0.2 C-rate using a Sb_2O_3 coated separator, the cathode was recovered and the charge was carried out in N_2 atmosphere at 5 °C min^{-1} from room temperature to 200 °C.

1.3 Electrochemical measurements

To confirm the electrochemical stability of the PE- and PI-based separators, a three-electrode cell was assembled with Li metal (reference and counter electrodes) and glassy carbon (working electrode) using a potentiostat (VSP, Biologic). The cell was scanned at 1 mV s^{-1} from the open circuit potential to 0.0 V (vs. Li/Li^+) to determine electrochemical reduction stability and electrochemically reduced by scanned at 1 mV s^{-1} to 4.5 V (vs. Li/Li^+).

A 2032 type full cell was manufactured to evaluate electrochemical performance. The full cell consists of $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (NCM811, L&F) cathode, natural graphite anode (BTR), electrolyte and separator (loading densities of NCM811 cathode and graphite anode were 7.12 and 4.17 mg cm^{-2}, respectively). After assembling the cells, they were aged for 12 hours. The cell was then charged from 2.8 V (vs. Li/Li^+) to 4.2 V (vs. Li/Li^+) for 2 cycles at 0.1 C (formation) and then from 3.0 V (vs. Li/Li^+) to 4.2 V (vs. Li/Li^+) were performed for 100 cycles at 1.0 C. Additionally, a water-containing electrolyte solution of 500 ppm was prepared to evaluate the electrochemical performance in the presence of excess H_2O and HF. A 2032 type full cell was manufactured and electrochemical evaluation was conducted under the same conditions as above.

The cycled cathode surface and morphology were analyzed using a Scanning Electron microscope (SEM). The chemical composition with the cycled cathode surface was analyzed using X-ray Photoelectron Spectroscopy (XPS). The fitting of each XPS peak was performed based on the C–C peak (285.0 eV).

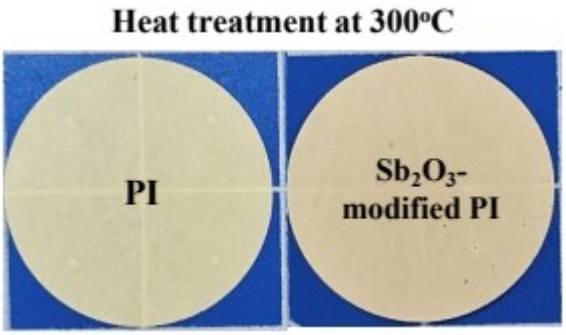

Figure S1. Shrinkage tests of the PI and Sb_2O_3-modified PI separators up to 300°C.

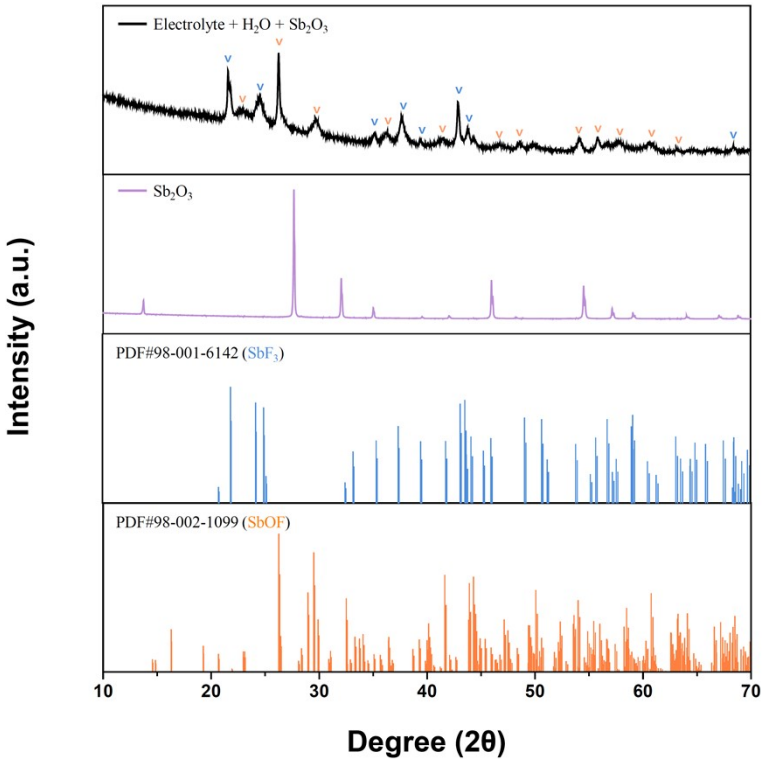

Figure S2. XRD results of Sb_2O_3 and solidified products after chemical reaction of electrolyte, H_2O, and Sb_2O_3.

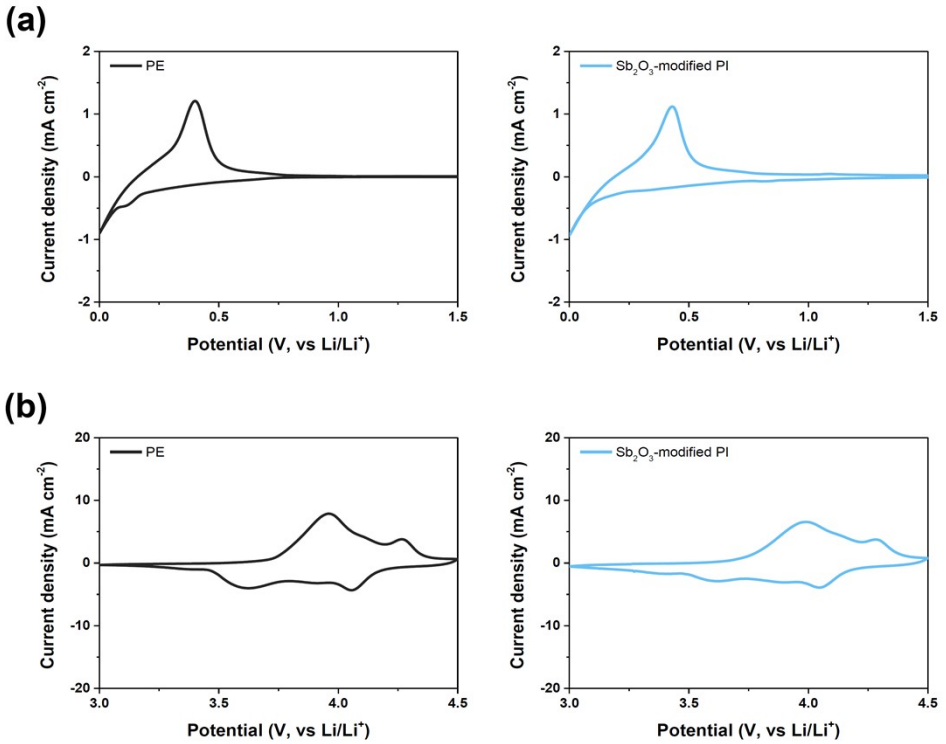

Figure S3. Cyclic voltammetry of the PI and Sb_2O_3-modified PI separators for (a) graphite anode and (b) NCM811 cathode.