Experimental supplementary information (ESI) available: Details of cell preparation, characterization.

Experimental Methods

Cell preparation: Ketjen black (KB, Lion Co.) was used as an electronic conductive additive.[1] Sulfur composite electrodes with KB and P_2S_5 (S-KB-P_2S_5) were prepared by mechanical milling of the mixture of S_8 (Aldrich, 99.5%), KB and P_2S_5 (Aldrich, 99%) with a weight ratio of 50 : 10 : 40. The rotation speed of disk and milling time were 370 rpm and 4 h.[3] All-solid-state Li/S cells with the S-KB-P_2S_5 composite electrode were assembled. The S-KB-P_2S_5 composite electrode (3 mg) as a working electrode and Li_3PS_4 glass electrolyte[4] as a separator layer were set in a polycarbonate tube (Φ10 mm) and pressed together under 360 MPa. Li-In alloy as a counter and reference electrode was placed on the surface of the solid electrolyte side of the bilayer pellet and pressed the three-layered pellet under 120 MPa. The electrochemical performance of the cells was examined at the constant current density of 0.64 mA cm^{-2} (0.1 C) at room temperature using a charge-discharge measuring device (VMP3, Bio-Logic Co.).

Characterization: ^{31}P magic-angle-spinning (MAS) NMR spectrum of the S-KB-P_2S_5

composite electrode is acquired at 160.26 MHz using a JEOL ECX-400 spectrometer, with a Φ4 mm ZrO_2 rotor at a 15 kHz spinning speed. The 90° pulse width and relaxation delay were 5 μs and 10 s, respectively. The accumulated number was 2048. The ^{31}P NMR spectra were referenced to external $(NH_4)H_2PO_4$ at 1.33 ppm. FE-SEM observation and EDX mapping of the S-KB-P_2S_5 composite electrode are conducted at the acceleration voltage of 3 kV and 15 kV using FE-SEM (SU-8220, HITACHI). XRD measurements of S-KB-P_2S_5 composite electrodes before and after the discharge-charge tests were conducted using a diffractometer (SmartLab, Rigaku) with CuKα radiation (40 kV, 200 mA). The existence of crystals in the S-KB-P_2S_5 composite electrodes after the discharge test was examined in detail by a transmission electron microscope (TEM, JEM- 2100F, JEOL) at an acceleration voltage of 200 kV. Electronic structures in the S-KB-P_2S_5 composite electrodes before and after the discharge-charge tests were analyzed by X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific) with a monochromatic AlKα source (1486.6 eV). The observed binding energies were calibrated with the adventitious C1s peak to 284.7 eV or KB peak to 284.2 eV.

References:

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