Solid electrolyte. The solid electrolyte, $Li_{10}GeP_2S_{12}$ (LGPS), used in this work was synthesized as previously described.

Cell Assembly. In this work, SSBs were assembled in a homemade cell casing, which has been shown in our previous work.15 The SEM, ADF-STEM images and the XPS characterization results of the coating layer could be found in Supporting Information, Figure S1 and S2. First, 80 mg of the LGPS powder were filled into the PEEK (polyether ether ketone) cylinder and cold pressed with 1 t for 1 min (10 mm diameter). The composite cathode was prepared by mixing c-LiCoO2 and SE in a weight ratio of 70 : 30 (corresponding to a volume ratio of 49 : 51) by hand. On one side of the pre-formed LGPS pellet, 10 mg of the composite cathode (corresponding to a loading of 1.1 mAh / cm2) was spread, followed by uniaxial pressing with 3.5 t for 2 min. On the other side of the SE pellet, either a thin indium foil with a diameter of 8 mm (Alfa Aesar, 99.99 %, 0.125 mm in thickness), or 20 mg of composite anode with Li4Ti5O12 : SE : C65 = 30 : 60 : 10 wt%, was attached, and then pressed with 1.5 t for 2 min, serving as anode of the SSB. Two stainless steel rods were fixed by screws to serve as current collectors. The total cell casing was subject to constant uniaxial pressure using the screw of an aluminum framework with 10 Nm torque (~ 70 MPa).

Electrochemical tests. Galvanostatic cycling of the cells was carried out in the voltage range of 2.0 – 3.6 V vs. In / InLi, or 1.1 – 2.7 V vs. $Li_4Ti_5O_{12}$ / $Li_7Ti_5O_{12}$, which corresponds to about 2.6 – 4.2 V against Li+ / Li. The theoretical capacity of $LiCoO_2$ was taken as 137 mAh / g, calculated based on $Li0.5CoO_2$ in the fully charged state. For all tests we used the VMP3 electrochemical workstation by Bio-Logic Science Instruments SAS. Electrochemical impedance spectroscopy (EIS) was carried out using the SP300 electrochemical workstation by Bio-Logic Science Instruments SAS. EIS spectra were always taken in the charged state (3.6 V vs. In / InLi) after selected cycles at 0.1 C. A rest period of 30 min was added before the EIS tests. An excitation voltage of 10 mV was chosen for measurements in the frequency range of 7 MHz – 10 mHz with 10 points per decade.

X-ray diffraction (XRD). X-ray diffraction was carried out with an Empyrean powder diffractometer (PANalytical, Netherlands) with Cu Ka radiation ()1 = 154.056 pm,)2 = 154.539 pm, I ()1 /)2 = 0.5). The cycled ASSB was disassembled inside the glovebox and the obtained pellet was sealed inside a silicon zero background sample holder covered with Kapton foil. All diffraction patterns were recorded in the 2θ range from 10 – 80 °, with a step size of 0.026 º and 300 s / step.

X-ray photoelectron spectroscopy (XPS). XPS measurements were carried out with a PHI Versaprobe II Scanning ESCA Microprobe (Physical Electronics PHI / ULVAC-PHI, USA) with a monochromatized Al Ka X-ray source (Beam area 200 µm × 1400 µm, X-ray power of 100 W). The pass energy of the analyzer was set to 23.5 eV for high-resolution spectra and to 187.6 eV for survey scans. For the pristine LGPS / LCO composite (without additional carbon) the C 1s signal from adventitious hydrocarbons was set to 284.8 eV to correct for charging effects. This resulted in a binding energy of 26.2 eV for the Ta 4f7/2 signal from the cathode coating layer (Ta5+), which then was used as reference for all samples. All thiophosphate-containing samples were transferred under an argon atmosphere to the vacuum chamber with an air-tight sample transfer vessel. The sample holder was cooled with liquid nitrogen to low temperature ranges (−60 to −80 ºC) throughout the whole measurement process, in order to

avoid possible sulfur evaporation from the SE. The CasaXPS software package (Version 2.3.17) was used for data analysis.

Scanning Transmission Electron Microscope (STEM). A small piece of composite cathode was removed from the solid-state cell in an argon filled glovebox, placed in a sample vial and crushed. Dry acetonitrile was added and the suspension was sonicated for 20 minutes to disperse the powder. The sample was transferred to TEM copper grids by dropping the suspension onto the grid and evaporating the solvent. The copper grid was transferred to the TEM holder using a nitrogen filled glove bag and the TEM holder was inserted rapidly into the microscope, minimizing air exposure. Annular dark field images and electron energy loss spectra were recorded using an aberration-corrected ARM200F STEM/TEM operating at 200 kV. The ADF micrographs were taken using a converge semi-angle of 22 mrad and collection angles of 54 - 276 mrad.

Scanning Electron Microscope (SEM) Secondary electron images were recorded on a Zeiss Merlin microscope at 3 kV acceleration voltage. Samples were fixed on conducting adhesive tape in an argon filled glovebox and moved to the microscope using a transfer chamber to avoid exposure to air.