Electronic Supporting Information (ESI)

Enhanced Li-Ion Conductivity in $LiBH_4$-ZrO_2 Nanocomposites and Nanoscale Li Imaging by Energy-Filtered Transmission Electron Microscopy

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Experimental Section

All samples were handled in an argon-filled glovebox with an O_2 level below 2 ppm. Micron ZrO_2 (~5 μm, purity 99%, Aldrich) and nano ZrO_2 (<100 nm, purity N.A., surface area ≥25 m^2/g, Aldrich) powders were used as received. Mechanical milling was performed using a planetary ball-milling apparatus (Fritsch, Pulverisette 7, Cr-steel vessel with 15 zirconia balls). The ball-to-powder weight ratio was 84:1. $LiBH_4$ (purity ≥ 95%, Aldrich) was ball-milled at 500 rpm for 2 h in an Ar atmosphere. Then, ball-milled $LiBH_4$ and each ZrO_2 powder were mixed using a volume ratio of 3:1 (weight ratio of 1:3) by ball-milling at 300 rpm for 0.5 h in an Ar atmosphere. Heat treatment of samples were performed by using thermogravimetry-differential thermal analysis (TG-DTA, Bruker, 2000SA) under Ar atmosphere. The samples were heated to 140 °C with the heating rate of 5 °C/min and were kept at 140 °C for 30 min. Crystalline phases of samples were analyzed by X-ray diffraction (XRD, Rigaku MiniFlex with Cu Kα radiation). The XRD samples were covered with a polyimide sheet in the glovebox to avoid contact with air. For ion conductivity measurements and scanning electron microscopy (SEM), sample powders were pressed into a pellet (7 mm, ~2 mm thick). Ion conductivities were measured using an alternating-current impedance analyzer (HIOKI IM3536, 4 Hz–8 MHz). Lithium foils (purity 99.9%, Alfa Aesar, thickness of 0.75 mm) were used as electrodes. The cross-sectional images of the pellets were observed by field emission gun SEM (FESEM, JEOL, JSM-7001FA) with an acceleration voltage of 15 kV. The cross-section of the pellets was obtained by cutting the sample using a pair of scissors in a glovebox. The samples were set on the specimen holder in the glovebox and then quickly transferred to the SEM chamber to minimize air exposure. Solid-state nuclear magnetic resonance (NMR) spectra were collected using a Bruker Avance Neo 500 spectrometer in a magnetic field of 11.74 T. Information about Li ion dynamics was collected using static ^7Li spectra. The 2.5 mm Bruker ZrO_2 rotors were filled with sample powders. The spectra were acquired in a single-pulse experiment with a pulse width of 4.0 μs. The chemical bonding states were analyzed by ^6Li and ^{11}B magic angle spinning (MAS) NMR spectra. The 3.2 and 2.5 mm ZrO_2 rotors were filled with sample powders for the ^6Li and ^{11}B MAS spectra measurements, respectively. The ^6Li and ^{11}B MAS spectra were recorded with spinning speeds of 20 and 15 kHz, respectively. Chemical shifts were calibrated using 1.0 M aqueous solutions of LiCl for ^6Li and $NaBH_4$ for ^{11}B. The ^6Li and ^{11}B MAS spectra were acquired with pulse lengths of 1.6 and 1.4 μs, and delay times of 10–30 and 5 s, respectively. Transmission electron microscopy (TEM) observations were conducted by Cs-corrected STEM (FEI, Titan) with an acceleration voltage of 300 kV. The sample powders were dispersed on a carbon film-coated grid (quantifoil) or a holey silicon nitride film-coated grid. Then, the grid was set to an Atmos Defend Holder (Phyla, Mel-Build) in the glovebox to transfer the specimen without exposure to air. Energy-filtered TEM (EFTEM) images were acquired using the elastic electrons, Li K-edge, B K-edge, and Zr $M_{4,5}$-edge. The energies of the Li K-edge, B K-edge, and Zr $M_{4,5}$-edge were 55, 188, and 180–182 eV, respectively. The three-window method was applied for the elemental mapping. The Li mapping was acquired with Li K-edge by inserting a slit length of 10 eV and using an exposure time of 5-30 s. Considering the close energies between the B K-edge and Zr $M_{4.5}$-edge, the combined mapping from B and Zr was acquired with the Zr $M_{4,5}$-edge by inserting a slit length of 20 eV and using an exposure time of 30-60 s. The energy-dispersive X-ray spectroscopy (EDS) analysis in STEM mode was performed using a beam current of 50 pA. TEM-electron energy loss spectra (EELS) were taken for the selected sample area.

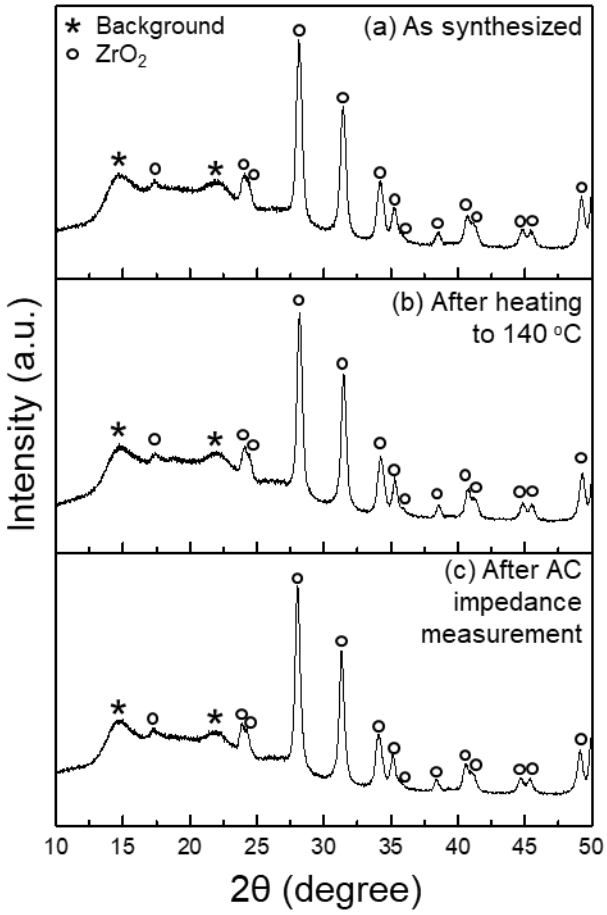

Fig. S1 XRD profiles of 25 vol.% nano ZrO_2 composite: (a) as synthesized, (b) after heating to 140 °C under Ar atmosphere, (c) after AC impedance measurements up to 140 °C.

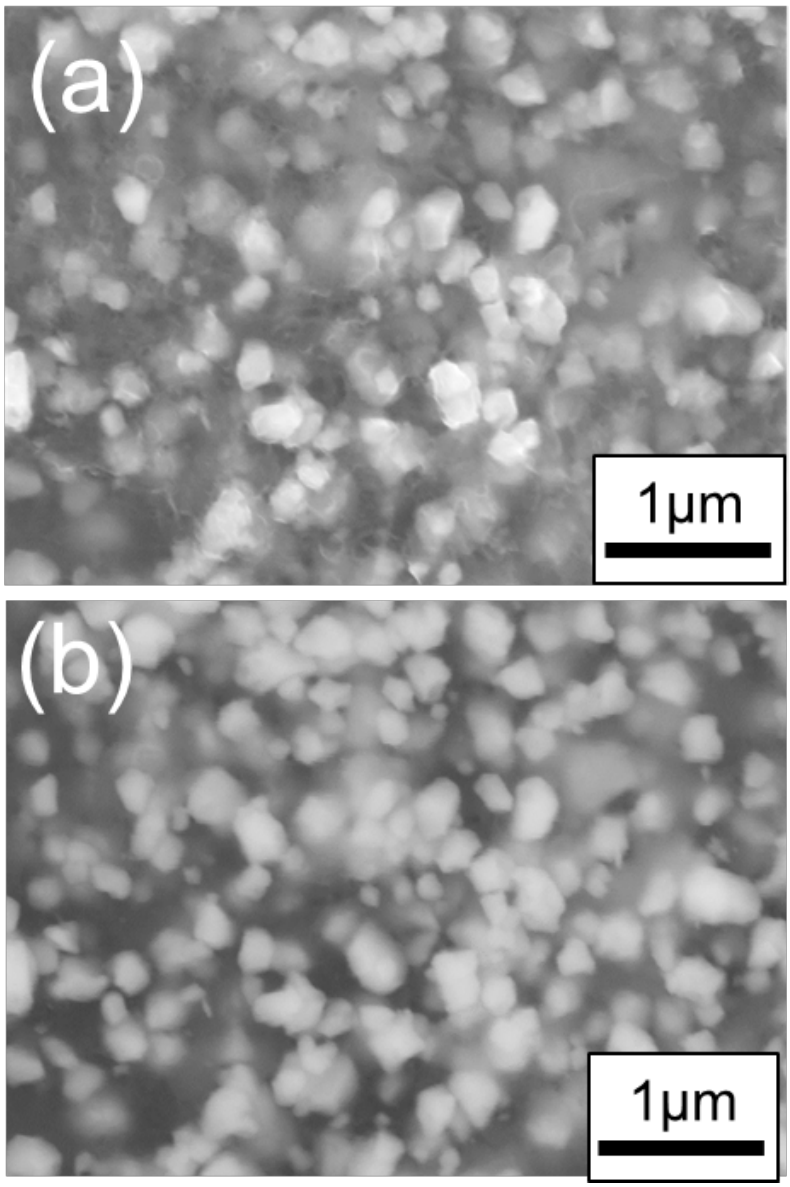

Fig. S2 Cross-sectional SEM images of 25 vol.% micron ZrO_2 composite pellets: (a) secondary electron image and (b) backscattered electron image.

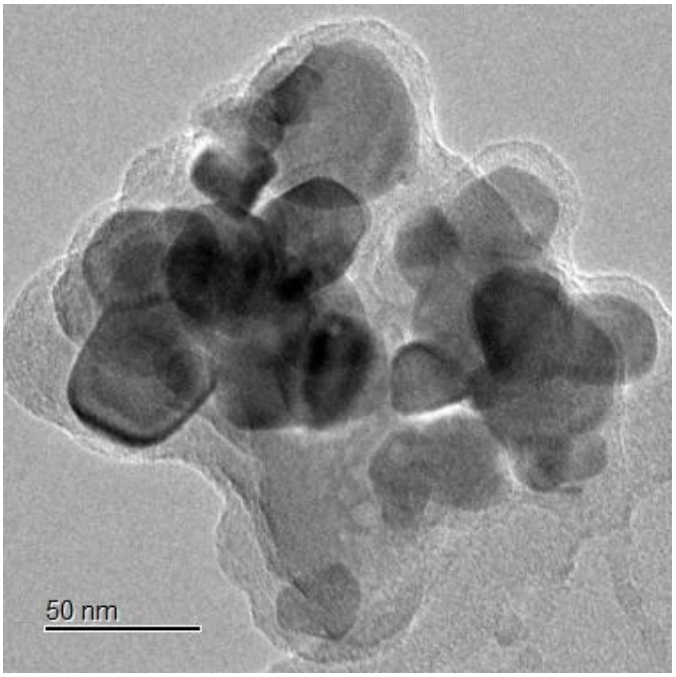

Fig. S3 The corresponding unfiltered TEM image for 25 vol.% nano ZrO_2 composite.

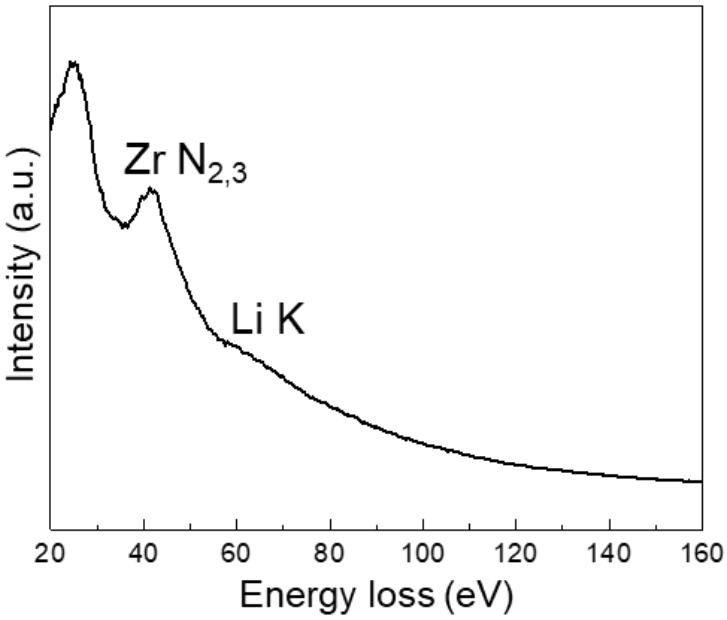

Fig. S4 TEM-EELS spectrum of as-synthesized 25 vol.% nano ZrO_2 composite.

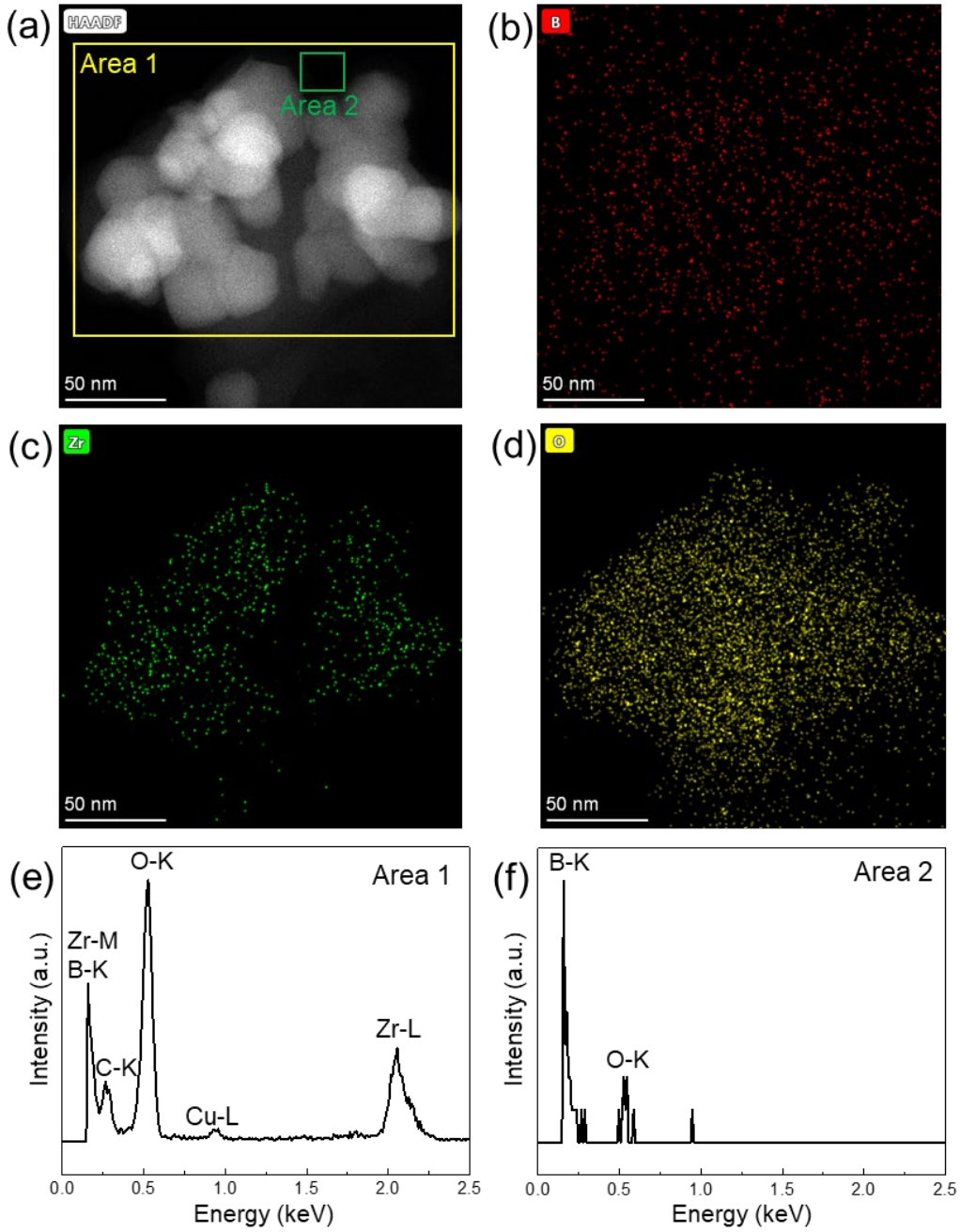

Fig. S5 (a) HAADF-STEM image, (b) EDS mapping of B, (c) EDS mapping of Zr, (d) EDS mapping of O, (e) EDS spectrum of area 1 in Fig. S5(a), and (f) EDS spectrum of area 2 in Fig. S5(a).

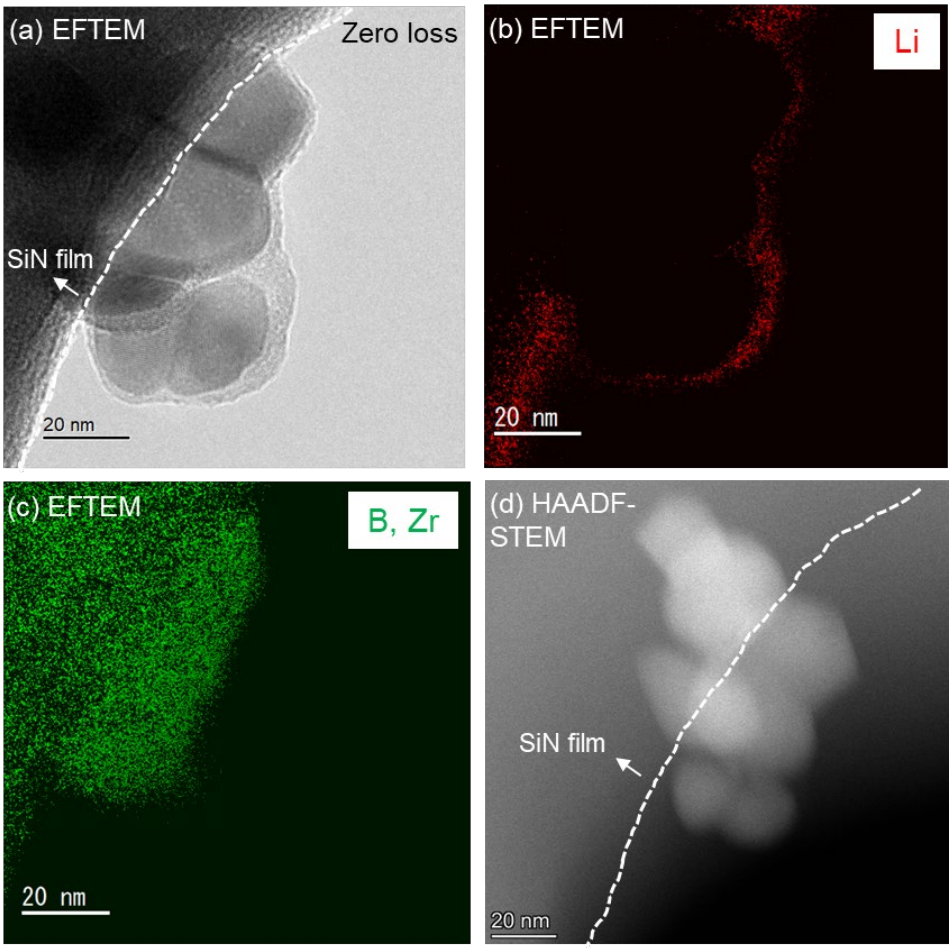

Fig. S6 (a) EFTEM zero-loss image, (b) EFTEM Li mapping, (c) EFTEM combined elemental mapping from B and Zr, and (d) HAADF-STEM image for 25 vol. % nano ZrO_2 composite after ion conductivity measurements (heating to 140 °C). The Li K-edge was used for Li mapping, and the B K-edge and Zr $M_{4,5}$-edge were used for the combined mapping. The particles were deposited on holey SiN films on the TEM grids, which is indicated in the upper-left corner of the images. The thickness of SiN film was ~200 nm.