Supplementary Materials for

A reversible oxygen redox reaction in bulk-type all-solid-state batteries

Kenji Nagao, Yuka Nagata, Atsushi Sakuda*, Akitoshi Hayashi, Minako Deguchi, Chie Hotechama, Hirofumi Tsukasaki, Shigeo Mori, Yuki Orikasa, Kentaro Yamamoto, Yoshiharu Uchimoto, Masahiro Tatsumisago

*Corresponding author. Email: saku@chem.osakafu-u.ac.jp

Published 19 June 2020, Sci. Adv. 6, eaax7236 (2020)
DOI: 10.1126/sciadv.aax7236

This PDF file includes:

Supplementary Text
Figs. S1 to S10
References
Supplementary text

Crystal structural analysis of Li$_2$RuO$_3$-Li$_2$SO$_4$ positive electrode materials

The Li$_{2}$Ru$_{1-x}$S$_x$O$_{3+x}$ positive electrode materials were synthesized by mechanochemical reaction of Li$_2$RuO$_3$ and Li$_2$SO$_4$ crystals. Fig. S1A shows the XRD patterns for the synthesized Li$_2$Ru$_{1-x}$S$_x$O$_{3+x}$ (x = 0, 0.1, 0.2, 0.3, 0.4, and 0.5) positive electrode materials. After the mechanochemical treatment with Li$_2$SO$_4$, layered Li$_2$RuO$_3$ transformed to disordered rocksalt phase. Obvious peak shift was not observed even when the Li$_2$SO$_4$ content was altered. This result provides clear evidence that the solid solution of Li$_2$RuO$_3$ and Li$_2$SO$_4$ is not formed and that Li$_2$SO$_4$ forms the amorphous matrix. In order to study the detail crystal structure, Rietveld refinement for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode material was carried out. Fig. S1B shows the results for the refinement as assuming S$^{6+}$ ions can occupy the octahedral site in rocksalt structure. In this case, the lattice parameter and the occupancy for the S$^{6+}$, Ru$^{4+}$, and Li$^+$ ions were refined. However, only a slight sulphide ion can occupy the octahedral 4a site, which means that Li$_2$SO$_4$ mainly forms amorphous matrix. Fig. S1C shows the results as assuming they do not occupy. In this study, the other parameters such as the isotropic thermal parameters (U) was not refined. Good refinement result was also obtained although the XRD profile showed the wide crystalline peaks. Moreover, we calculated the XRD pattern for the case which the S$^{6+}$ ion occupies the octahedral site. As shown in Fig. S1D, with an increase in sulphide occupancy, electron density in the transition metal layer decreases, which leads to the decrease of intensity in some diffraction peaks. This is because electron density in the 111 plane decreases because of the substitution of the S$^{6+}$ ion with the Ru$^{4+}$ ion in the rocksalt structure. Therefore, the intensity ratio (111/200) is expected to decrease as a result of the sulphur substitution. However, in the obtained XRD patterns shown in Fig. S1A, the ratio has never changed even in the case where the sulphate content was altered, which implies that sulphur does not occupy the octahedral site. Moreover, the ionic radius of S$^{6+}$ ion (r = 0.29 Å) in the octahedral environment is smaller than that of the Ru$^{4+}$ (r = 0.62 Å) ion, such that the lattice would be shrunk and the Bragg peak shifted towards lower angles if the substitution had occurred \((39)\). Moreover, TEM observation was done for the disordered Li$_2$RuO$_3$ after ball milling. Fig. S2 shows the BF- and DF-TEM images, HR-TEM image, ED patterns and corresponding intensity profiles for disordered Li$_2$RuO$_3$. In the HR-TEM image, amorphous and crystalline regions were confirmed as the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$. Obvious Bragg peak shift was not observed in the intensity profile shown in Figs. S2D and S2E. Considering above results, we conclude that solid solution do not be formed and the Li$_2$SO$_4$ component exists as an amorphous matrix.
Fig. S1 Structural analyses for the Li$_2$RuO$_3$-Li$_2$SO$_4$ system positive electrode active materials prepared by ball-milling. (A) X-ray diffraction patterns for the (100-x)Li$_2$RuO$_3$·xLi$_2$SO$_4$ (mol%) positive electrode active materials. At all the compositions, cation-disordered rock-salt phase was obtained, while RuO$_2$ crystal was precipitated as an impurity phase at the Li$_2$RuO$_3$ composition. (B) Rietveld refinement for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ (x = 20) positive electrode material. The Rietveld refinement was carried out as assuming sulphide ions can occupy the octahedral site in rocksalt structure. The lattice parameter and the occupancy for the sulphide and ruthenium ions were refined. However, only a slight sulphide ion can occupy the octahedral site, which means that Li$_2$SO$_4$ mainly forms amorphous matrix. (C) Rietveld refinement for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode material. The Rietveld refinement was carried out as assuming sulphide ions do not occupy the octahedral site in rocksalt structure. (D) Simulated XRD patterns for the Li$_{0.66}$Ru$_{0.33}$S$_{1.5}$O rocksalt structure. As assuming sulphide ion can occupy the octahedral site in rocksalt structure, XRD pattern was simulated.
Fig. S2 TEM observation for the Li$_2$RuO$_3$ after the mechanical milling treatment. (A) Bright-field TEM image and (B) dark-field TEM image for disordered Li$_2$RuO$_3$. In the DF-TEM image, the bright spots (crystalline) and the dark region (amorphous) were clearly observed. (C) High resolution-TEM image with corresponding fast Fourier transform images for disordered Li$_2$RuO$_3$. (D and E), Electron diffraction pattern and corresponding intensity profile for disordered Li$_2$RuO$_3$ and Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$. In the both cases, the same profiles were observed. This results also support that the obtained nanocrystal was assigned to cation-disordered rocksalt phase.
Relationship between charge-discharge capacity and the ductility and conductivity of Li$_2$RuO$_3$-Li$_2$SO$_4$ positive electrode active materials

In order to understand the charge-discharge capacity obtained in Li$_2$RuO$_3$-Li$_2$SO$_4$ positive electrodes, ductility and conductivity in the compressed powder were investigated. Electronic and ionic conductivities were measured by the DC polarization technique as shown in Fig. S3. Figs. S3A and S3B show the AC impedance plot and DC polarization curves for the Au/Li$_3$PS$_4$/Au cell to measure ionic and electronic conductivities for the Li$_3$PS$_4$ electrolyte, respectively. These conductivities are summarized as Arrhenius plots shown in Fig. S3C. Even at a high temperature, the Li$_3$PS$_4$ glass electrolyte exhibited an extremely low electronic conductivity besides a high lithium ionic conductivity, thus Li$_3$PS$_4$ was used as an electron blocking layer for the ionic conductivity measurement for the Li$_2$RuO$_3$-Li$_2$SO$_4$ electrodes. Fig.S3D shows the AC impedance plots and DC polarization curve for the Au/LiRu$_{0.5}$S$_{0.5}$/Au cell. From these measurements, it was found that the synthesized Li$_2$RuO$_3$-Li$_2$SO$_4$ electrodes have high electronic conductivity. In order to measure the ionic conductivity for the Li$_2$RuO$_3$-Li$_2$SO$_4$ electrodes, the five layered cells (Li/Li$_3$PS$_4$/Li$_2$RuO$_3$-Li$_2$SO$_4$/Li$_3$PS$_4$/Li) were fabricated and the ionic conductivity was measured from AC impedance and DC polarization techniques. Fig. S3E shows the AC impedance plots for the five layered cell. Semicircles attributable to the bulk resistance of the Li$_3$PS$_4$ layers and interfacial resistance between Li$_2$RuO$_3$-Li$_2$SO$_4$/Li$_3$PS$_4$ interfaces were observed in the high frequency region. However, these values was enough small compared to the bulk resistance in the synthesized electrode materials, therefore these values were neglected for the calculation of the ionic conductivity for the Li$_2$RuO$_3$-Li$_2$SO$_4$ electrode materials. The ionic conductivity was calculated from the current at the equilibrium state after the polarization.

Fig. S4A shows the cross-sectional SEM images for the Li$_2$RuO$_3$-Li$_2$SO$_4$ green compacts after pressing the powders under 540 MPa at room temperature. In the SEM images, the volumetric fraction of grain boundary decreases with an increase in the Li$_2$SO$_4$ content. Because of the existence of Li$_2$SO$_4$ in amorphous matrix, ductility in the active materials improves and densification, i.e. “room temperature pressure sintering” proceeds (22). Fig. S4B describes the relationship between Li$_2$SO$_4$ content and the relative density for the green compacts. With increases in the Li$_2$SO$_4$ content in (1-x)Li$_2$RuO$_3$:xLi$_2$SO$_4$, the relative density increases, which means that ductility of the active materials improves, supporting results in the SEM observation. Fig. S4C shows the composition dependence of electronic and ionic conductivity for (1-x)Li$_2$Ru$_{0.5}$O$_{3-x}$Li$_{2.5}$S$_{4}$O$_{4}$. Electronic conductivity increases even when electronic insulating Li$_2$SO$_4$ is added, caused by further densification and the decrease of grain boundary. At the x = 0.5 composition, electronic conductivity dramatically decreases due to the lower content of transition metal ions. On the other hand, ionic conductivity increases with increases in the Li$_2$SO$_4$ ratio in the region of 0 ≤ x ≤ 0.4 because of the enhancement in ductility and the mixed anion effect in the amorphous matrix (40). At the x = 0.5 composition, conductivity decreases due to the remaining Li$_2$SO$_4$ in the crystal, which is confirmed by XRD.

Charge-discharge curves of all-solid-state cells using the (1-x)Li$_2$Ru$_{0.5}$O$_{3-x}$Li$_{2.5}$SO$_{4}$. The first charge-discharge capacity and Li$_2$SO$_4$ content is shown as Fig. S4D. Relationship between discharge capacity and Li$_2$SO$_4$ content is shown as Fig. S4E. In the region of 0 ≤ x ≤ 0.2, the charge-discharge capacity increases with increasing Li$_2$SO$_4$ content. By increasing the Li$_2$SO$_4$ content, ductility and conductivity increases, and thus many more lithium ions in the Li$_2$RuO$_3$ can be extracted or inserted, increasing the capacity. In the Li$_2$Ru$_{0.8}$SO$_{4.2}$O$_{3.2}$, almost all lithium ions in Li$_2$RuO$_3$ are extracted/inserted, and the highest capacity is obtained. Moreover, in the 0.2 ≤ x ≤ 0.4 region, the charge-discharge capacity gradually decreases. This is because the content in Li$_2$RuO$_3$, which is the redox active component,
decreases. In this region, ionic conductivity is high enough for achieving high capacity, and therefore, all lithium ions in the Li$_2$RuO$_3$ structure are likewise fully extracted, and almost the theoretical capacity is achieved. At the $x = 0.5$ composition, although the ductility is high, conductivity is quite lower than that of the other cases. This low conductivity prevents the extraction of lithium ions from the structure, thus only limited capacity is obtained.

Fig. S4F shows the cross-sectional SEM image for the all-solid-state cell using the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode. Thickness of the positive electrode is estimated to about 100 μm.
Fig. S3 Conductivity measurements for the Li$_2$RuO$_3$-Li$_2$SO$_4$ materials by using electrochemical techniques. (A) AC impedance plots and (B) DC polarization curves for the symmetric cell (Au/Li$_3$PS$_4$/Au) at 25 °C and 100 °C. (C) Arrhenius plot for the calculated ionic and electronic conductivities for Li$_3$PS$_4$ glass electrolyte. The ionic and electronic conductivities of the Li$_3$PS$_4$ glass electrolyte were, respectively, 4.8×10$^{-4}$ S cm$^{-1}$ and 5.5×10$^{-7}$ S cm$^{-1}$ at 25 °C. By elevating the temperature to 100 °C, the glass electrolyte showed the ionic conductivity of 9.8×10$^{-3}$ S cm$^{-1}$ and the electronic conductivity of 7.6×10$^{-7}$ S cm$^{-1}$. (D) AC impedance plots and DC polarization curve for the symmetric cells (Au/Li$_3$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$/Au). (E) AC impedance plots and DC polarization curve for the symmetric cells (Li/Li$_3$PS$_4$/Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$/Li$_3$PS$_4$/Li) at 25 °C.
Fig. S4 Mechanical and electrochemical performance of the (1-x)Li$_2$RuO$_3$-xLi$_2$SO$_4$ (molar ratio) active materials. (A) Cross-sectional SEM images of the powder-compressed pellets. (B) Composition dependence of the powder density and relative density of the Li$_2$RuO$_3$-Li$_2$SO$_4$. The pellets were obtained by pressing the powder under 540 MPa at room temperature. Powder density was measured by using Ar gas pycnometer placed in Ar filled grove box. Relative density was calculated by dividing the density of green compacts by their powder density. (C) Electronic and lithium ionic conductivities of the Li$_2$RuO$_3$-Li$_2$SO$_4$ at room temperature. (D) Charge-discharge curves of all-solid-state cells operated under the constant current density of 0.25 mA cm$^2$ in the voltage range of 1.6-4.8 V vs. Li at 100 °C. (E) Relationship between the obtained capacity and the Li$_2$SO$_4$ content in the active materials. The highest reversible capacity was obtained at the x = 0.2 composition. In the composition range of 0.2 ≤ x ≤ 0.4, capacity which is almost matched with the theoretical capacity based on the Li$_2$RuO$_3$ component was obtained. (F) Cross-sectional SEM image for the all-solid-state cell using Li$_2$Ru$_{0.8}$SO$_{2.2}$O$_{3.2}$ positive electrode. After assembling the pelletized cell, the cell was broken and the cross-section was exposed. Then, the cross-section was polished by Ar$^+$ milling. Dense positive electrode layer composed of only the Li$_2$Ru$_{0.8}$SO$_{2.2}$O$_{3.2}$ active material with approximately 100 μm was obtained just by pressing at room temperature.
Electrochemical analysis of the composite electrode based on Li$_2$RuO$_3$ (C2/c) active material

Electrochemical analyses were likewise carried out for the all-solid-state cell with the composite positive electrode based on Li$_2$RuO$_3$ active material and the Li$_3$PS$_4$ glass electrolyte, to be compared with the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode. Results are shown in Fig. S5. Charge-discharge curves for the all-solid-state cell using a composite electrode of crystalline Li$_2$RuO$_3$ (C2/c) electrode active material and Li$_3$PS$_4$ electrolyte operated at 100 °C under the constant current density of 0.25 mA cm$^{-2}$ are shown in Fig. S5A. GITT curves for the all-solid-state cell at the initial and second cycles are shown as Fig. S5B and S5C, respectively. At the initial charging state, obvious voltage plateau due to oxygen oxidation reaction was observed, but it disappeared at the second cycle. Fig. S5D shows cross-sectional SEM images and corresponding EDX mappings for the constitute elements. Thickness of the composite positive electrode layer was about 100 μm. Well-contacted electrode/electrolyte interface was successfully obtained just by pressing at room temperature.

In order to understand the detail charge-discharge mechanism for crystalline Li$_2$RuO$_3$ electrode active material in all-solid-state cell, GITT-AC impedance measurements were carried out (Figs. S5E-S5F). In the AC impedance plots, there are three characteristic resistance components in the high, middle and low frequency region, denoted $R_1$, $R_2$ and $R_3$, respectively. $R_1$ is attributable to the resistance of the solid electrolyte in the separator layer. $R_2$ and $R_3$ is presumably assigned to the charge transfer resistance between Li$_2$RuO$_3$ active materials and the Li$_3$PS$_4$ glass electrolyte. According to Tarascon’s report (13), there are also three resistance components in the cell based on Li$_2$Ru$_{0.75}$Sn$_{0.25}$O$_3$ active material with organic liquid electrolyte. The reason for the interfacial resistance being described by two components has not been described yet, however, in the cell with the composite electrode based on Li$_2$RuO$_3$ active material, these interfacial resistances gradually increase with an increase in the state of charge during the early charging states where the cationic oxidation reaction mainly occurs. Moreover, during the latter charging states where anionic oxidation occurs, these resistances exponentially increase. This substantial resistance is the reason why the capacity in the anionic redox region is lower than expected. The diffusion coefficient is changed with increasing state of charge in the charging state. This behaviour has almost the same tendency as found in the previous report on the electrochemical analysis on Li$_2$Ru$_{0.75}$Sn$_{0.25}$O$_3$ by Tarascon et al. (13).
**Fig. S5**  Electrochemical analyses for the layered Li$_2$RuO$_3$ (C2/c) positive electrode active material in the all-solid-state cells. (A) Charge-discharge curves for the all-solid-state cell using the composite positive electrode of Li$_2$RuO$_3$ active material and Li$_3$PS$_4$ electrolyte operated at 100°C. (B) GITT curves of the all-solid-state cell at the initial cycle. (C) GITT curves of the all-solid-state cell at the second cycle. The red and blue curves indicate the charge and discharge ones, respectively. (D) Cross-sectional SEM images for the all-solid-state cell based on the composite
electrode and the corresponding EDX mappings for the constituent elements. Thickness of the composite positive electrode is estimated to be ca. 100 µm where the loading amount of the composite electrode was about 25 mg/10 mmφ. Magnified cross-sectional SEM images for the composite positive electrode, and corresponding EDX mappings of the Ru and O for Li$_2$RuO$_3$ active material and P and S for Li$_3$PS$_4$ glass electrolyte. (E) GITT curve and corresponding the mean diffusion coefficient ($D \cdot R^2$) and resistance in the initial charging state. (F) AC impedance plots at the various SOC. (G) GITT curve and corresponding the $D \cdot R^2$ and $R_{SE}$ in the initial discharging state.
Energy density calculation for the all-solid-state battery
A gold thin-film is inserted between the metallic lithium negative electrode and Li$_3$PS$_4$ glass electrolyte layers to suppress the dendritic growth of lithium (23). This battery exhibited a large reversible capacity of around 225 mAh g$^{-1}$ and a good cycle performance. The gravimetric energy densities based on the positive electrode weight was calculated to 665 Wh kg$^{-1}$ and it based on the battery weight (positive/negative electrodes and solid electrolyte) was 220 Wh kg$^{-1}$. Here, we have demonstrated the all-solid-state battery using the novel Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode active material, and this battery configuration is the favorable one for the high energy density.

Fig. S6  Bulk-type all-solid-state battery using the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode and metallic lithium negative electrode. (A) Charge-discharge curves of the all-solid-state Li/Au/Li$_3$PS$_4$/Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ battery. (B) cycle performance of the battery. (C) Configuration of the battery and the calculation of energy density. A gold thin-film was inserted between the metallic lithium negative electrode and Li$_3$PS$_4$ glass electrolyte layers to suppress the dendritic growth of lithium. This battery exhibited a large reversible capacity of around 224.5 mAh g$^{-1}$ and a good cycle performance. The gravimetric energy densities based on the positive electrode weight was calculated to 664.5 Wh kg$^{-1}$ and it based on the battery weight (positive/negative electrodes and solid electrolyte) was 220.3 Wh kg$^{-1}$.
Electrochemical analysis for the all-solid-state cell based on the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode in reversible cycles

Electrochemical analyses were also carried out for the all-solid-state cell with the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode in the reversible cycle. In the dQ/dV plots, shown in Fig. S7C, there are two characteristic peaks attributed to cationic and anionic redox reactions. The voltage hysteresis in the cationic and anionic redox region are 0.38 V and 0.45 V, respectively. In order to remove the kinetic contribution on the hysteresis, thermodynamic redox potential on the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode during the charge-discharge process was investigated using the GITT measurement. Even when the kinetic effect has been eliminated, the potential hysteresis persists as shown in Fig. S7A and S7B. The average voltage gap between charge and discharge curves in the second cycle was 0.33 V, which was lower than that of the previously reported lithium-excess positive electrode materials.

In order to investigate the redox mechanism in Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ in detail, alterations in resistance and diffusion properties were evaluated. As shown in Fig. 3, the interfacial resistance was clearly observed in the initial charge-discharge process, however, in the second charge-discharge process, no interfacial resistance and only spike behaviour was observed, as shown in Fig. S7D-S7G. This result indicates that an effective interlayer for charge-transfer has been created as a result of the activation of lithium-excess electrode materials during the initial charge-discharge process. Moreover, as interfacial resistance has never observed in the reversible cycles, the rate-limiting process is not the charge transfer but lithium diffusion in the active material. This is one of the reasons why the high capacity has obtained reversibly in all-solid-state cells. In addition, the diffusion coefficient gradually decreased during charging, but returned to the initial state by a different route during discharging. This is another reason behind the voltage hysteresis.
Fig. S7 Electrochemical analysis on the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode in all-solid-state cells. (A) GITT curve for the all-solid-state cells based on the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode at the initial cycle. (B) GITT curves of all-solid-state cells at the second cycle. (C) dQ/dV plots for the all-solid-state cell using Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode at the 5th cycle. (D) GITT curve and corresponding the mean diffusion coefficient ($D$-$R^2$) and resistance in the second charging state. (E) AC impedance plots at the various SOC. (F) GITT curve and corresponding the $D$-$R^2$ and R$^{SE}$ in the second discharging state. (G) AC impedance plots at the various depth of discharge (DOD).
Structural change of Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode during charge-discharge measurements

To understand the structural change in Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode, *ex-situ* XRD measurement was carried out. After charging/discharging to various state of charge (Fig. S8A), the all-solid-state cells were disassembled and the surface Au layer as a current collector was removed by polishing by using sand paper as shown in Fig. S8B. Then, XRD measurement was carried out for the polished surface. Fig. S8C and S8D show the XRD patterns for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode during charging and discharging, respectively. Intensity of diffraction peaks for the rocksalt structure decreased by the extraction of lithium ions, however, the peak shift was not observed in the initial charging state (0–33% charging). In this region, capacity is mainly caused by the charge compensation of the cationic Ru$^{4+}$/Ru$^{5+}$ oxidation reaction, and therefore a drastic structural change did not occur. In the further charging state (66–100%), where charge compensation of the anionic oxygen oxidation reaction mainly occurs, a slight shift toward higher angles was detected. The rocksalt structure shrunk by about 2%. This volumetric change is small compared to other positive electrode active materials. Moreover, after being fully charged, the diffraction peaks disappeared and amorphization proceeded because of the anionic oxidation reaction with the distortion.

In the corresponding discharging state, diffraction peaks to disordered rocksalt phase first appeared again and shifted towards the lower angles. Moreover, in the subsequent discharge state, the obvious peak shift was not observed while the intensity of the peaks increased. After being fully discharged to 1.6 V vs. Li, the crystalline phase returned to the pristine sample before charging.
Fig. S8  *Ex-situ* XRD measurement for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode active material in all-solid-state cells.  
(A) The initial charge-discharge curves of the all-solid-state cell using the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode active material for the *ex-situ* XRD and XAFS measurements.  
(B) Schematic image of the all-solid-state cells for the measurements. The bilayer pellet of Li$_3$PS$_4$ / Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ was obtained by pressing these powders at room temperature under 540 MPa. An gold thin-film positive electrode current collector was deposited on the electrode surface by vacuum evaporation. After that, lithium and indium foils and copper current collector were attached to the electrolyte side and pressed at 120 MPa to form an alloy negative electrode. After the charge-discharge test, the gold thin-film current collector was removed by polishing the surface. The Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ electrode surface was exposed and the XRD and XAFS measurements were conducted for this surface.  
(C and D) *Ex-situ* XRD patterns for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode active material in the all-solid-state cells at the various state of charge and at the various depth of discharge, respectively.
**Electronic structural analysis for as-prepared Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode active material**

The Ru K-edge X-ray absorption near edge structure (XANES) spectra of the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ and Li$_2$RuO$_3$ ($Fm\overline{3}m$) is slightly different from the profile of the Li$_2$RuO$_3$ ($C2/c$) crystal as a starting material (Fig. S9A). The white line of the Ru K-edge spectra for Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ and Li$_2$RuO$_3$ ($Fm\overline{3}m$) is located at lower energy than that for the layered Li$_2$RuO$_3$ ($C2/c$) crystal, which means that the Ru$^{4+}$ ion was partially reduced after the high energy ball-milling treatment whether or not Li$_2$SO$_4$ was added.
Fig. S9. Electronic structural analysis using X-ray absorption fine structure (XAFS) measurement for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode material. Ru K-edge (A) XANES and (B) EXAFS spectra for the as-prepared Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ powder. As a reference, the spectra for the layered Li$_2$RuO$_3$ (C2/c), the disordered Li$_2$RuO$_3$ (Fm$ar{3}$m), Ru metal, RuO$_2$ and RuCl$_3$·nH$_2$O are shown in this figure. (C) Ru K-edge XANES and (D) EXAFS spectra for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ at the various charge states. (E) Ru K-edge XANES and (F) EXAFS spectra for the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ at the various discharge states.
Fig. S10. Structural model for crystalline and amorphous regions in the Li$_2$Ru$_{0.8}$S$_{0.2}$O$_{3.2}$ positive electrode material in charge-discharge processes.
REFERENCES AND NOTES

1. J.-M. Tarascon, M. Armand, Issues and challenges facing rechargeable lithium batteries. *Nature* **414**, 359–367 (2001).

2. J. Janek, W. G. Zeier, A solid future for battery development. *Nat. Energy* **1**, 16141 (2016).

3. A. Manthiram, X. Yu, S. Wang, Lithium battery chemistries enabled by solid-state electrolytes. *Nat. Rev. Mater.* **2**, 16103 (2017).

4. Y. Seino, T. Ota, K. Takada, A. Hayashi, M. Tatsumisago, A sulphide lithium super ion conductor is superior to liquid ion conductors for use in rechargeable batteries. *Energ. Environ. Sci.* **7**, 627–631 (2014).

5. N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kajiyama, Y. Kato, S. Hama, K. Kawamoto, A. Mitsui, A lithium superionic conductor. *Nat. Mater.* **10**, 682–686 (2011).

6. Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsui, M. Yonemura, H. Iba, R. Kanno, High-power all-solid-state batteries using sulfide superionic conductors. *Nat. Energy* **1**, 16030 (2016).

7. K. Mizushima, P. C. Jones, P. J. Wiseman, J. B. Goodenough, Li$_x$CoO$_2$ (0<x≤1): A new cathode material for batteries of high energy density. *Mater. Res. Bull.* **15**, 783–789 (1980).

8. T. Ohzuku, Y. Makimura, Layered lithium insertion material of LiCo$_{1/3}$Ni$_{1/3}$Mn$_{1/3}$O$_2$ for lithium-ion batteries. *Chem. Lett.* **30**, 642–643 (2001).

9. M. H. Rossouw, M. M. Thackeray, Lithium manganese oxides from Li$_2$MnO$_3$ for rechargeable lithium battery applications. *Mater. Res. Bull.* **26**, 463–473 (1991).

10. A. C. W. P. James, J. B. Goodenough, Structure and bonding in lithium ruthenate, Li$_2$RuO$_3$. *J. Solid State Chem.* **74**, 287–294 (1988).

11. M. Sathiya, A. M. Abakumov, D. Foix, G. Rousse, K. Ramesha, M. Saubanère, M. L. Doublet, H. Vezin, C. P. Laisa, A. S. Prakash, D. Gonbeau, G. VanTendeloo, J.-M. Tarascon, Origin of voltage decay in high-capacity layered oxide electrodes. *Nat. Mater.* **14**, 230–238 (2015).

12. M. Sathiya, G. Rousse, K. Ramesha, C. P. Laisa, H. Vezin, M. T. Sougrati, M.-L. Doublet, D. Foix, D. Gonbeau, W. Walker, A. S. Prakash, M. Ben Hassine, L. Dupont, J.-M. Tarascon, Reversible anionic redox chemistry in high-capacity layered-oxide electrodes. *Nat. Mater.* **12**, 827–835 (2013).
13. G. Assat, C. Delacourt, A. D. Corte, J.-M. Tarascon, Practical assessment of anionic redox in Li-rich layered oxide cathodes: A mixed blessing for high energy Li-ion batteries. *J. Electrochem. Soc.* **163**, A2965–A2976 (2016).

14. J. Lee, A. Urban, X. Li, D. Su, G. Hautier, G. Ceder, Unlocking the potential of cation-disordered oxides for rechargeable lithium batteries. *Science* **343**, 519–522 (2014).

15. D.-H. Seo, J. Lee, A. Urban, R. Malik, S. Kang, G. Ceder, The structural and chemical origin of the oxygen redox activity in layered and cation-disordered Li-excess cathode materials. *Nat. Chem.* **8**, 692–697 (2016).

16. N. Yabuuchi, M. Takeuchi, M. Nakayama, H. Shiba, M. Ogawa, K. Nakayama, T. Ohta, D. Endo, T. Ozaki, T. Inamasu, K. Sato, S. Komaba, High-capacity electrode materials for rechargeable lithium batteries: Li$_3$NbO$_4$-based system with cation-disordered rocksalt structure. *Proc. Natl. Acad. Sci. U.S.A.* **112**, 7650–7655 (2015).

17. N. Yabuuchi, M. Nakayama, M. Takeuchi, S. Komaba Y. Hashimoto, T. Mukai, H. Shiba, K. Sato, Y. Kobayashi, A. Nakao, M. Yonemura, K. Yamanaka, K. Mitsuhasha, T. Ohta, Origin of stabilization and destabilization in solid-state redox reaction of oxide ions for lithium-ion batteries. *Nat. Commun.* **7**, 13814 (2016).

18. M. Tatsumisago, R. Takano, K. Tadanaga, A. Hayashi, Preparation of Li$_3$BO$_3$-Li$_2$SO$_4$ glass-ceramic electrolytes for all-oxide lithium batteries. *J. Power Sources* **270**, 603–607 (2014).

19. K. Nagao, A. Hayashi, M. Deguchi, H. Tsukasaki, S. Mori, M. Tatsumisago, Amorphous LiCoO$_2$-Li$_2$SO$_4$ active materials: Potential positive electrodes for bulk-type all-oxide solid-state lithium batteries with high energy density. *J. Power Sources* **348**, 1–8 (2017).

20. K. Nagao, A. Sakuda, A. Hayashi, H. Tsukasaki, S. Mori, M. Tatsumisago, Amorphous Ni-Rich Li$_{(Ni_{1−x}Mn_{x})O_2}$–Li$_2$SO$_4$ positive electrode materials for bulk-type all-oxide solid-state batteries. *Adv. Mater. Inter.* **6**, 1802016 (2019).

21. Y. Iriyama, T. Kako, C. Yada, T. Abe, Z. Ogumi, Charge transfer reaction at the lithium phosphorus oxynitride glass electrolyte/lithium cobalt oxide thin film interface. *Solid State Ion.* **176**, 2371–2376 (2005).

22. A. Sakuda, A. Hayashi, M. Tatsumisago, Sulfide solid electrolyte with favorable mechanical property for all-solid-state lithium battery. *Sci. Rep.* **3**, 2261 (2013).

23. A. Kato, M. Suyama, C. Hotehama, H. Kowada, A. Sakuda, A. Hayashi, M. Tatsumisago, High-temperature performance of all-solid-state lithium-metal batteries having Li/Li$_3$PS$_4$ interfaces modified with Au thin films. *J. Electrochem. Soc.* **165**, A1950–A1954 (2018).
24. K. M. Shaju, G. V. Subba Rao, B. V. R. Chowdari, Li ion kinetic studies on spinel cathodes, $\text{Li}(\text{M}_{1/6}\text{Mn}_{11/6})\text{O}_4$ ($\text{M} = \text{Mn, Co, CoAl}$) by GITT and EIS. *J. Mater. Chem.* **13**, 106–113 (2003).

25. A. Sakuda, A. Hayashi, M. Tatsumisago, Interfacial observation between LiCoO$_2$ electrode and Li$_2$S-P$_2$S$_5$ solid electrolytes of all-solid-state lithium secondary batteries using transmission electron microscopy. *Chem. Mater.* **22**, 949–956 (2010).

26. J. Haruyama, K. Sodeyama, L. Han, K. Takada, Y. Tateyama, Space-charge layer effect at interface between oxide cathode and sulfide electrolyte in all-solid-state lithium-ion battery. *Chem. Mater.* **26**, 4248–4255 (2014).

27. N. Ohta, K. Ohta, I. Sakaguchi, L. Zhang, R. Ma, K. Fukuda, M. Osada, T. Sasaki, LiNbO$_3$-coated LiCoO$_2$ as cathode material for all solid-state lithium secondary batteries. *Electrochem. Commun.* **9**, 1486–1490 (2007).

28. S. Hoshino, A. M. Glushenkov, S. Ichikawa, T. Ozaki, T. Inamasu, N. Yabuuchi, Reversible three-electron redox reaction of Mo$^{3+}$/Mo$^{6+}$ for rechargeable lithium batteries. *ACS Energy Lett.* **2**, 733–738 (2017).

29. A. Sakuda, T. Takeuchi, K. Okamura, H. Kobayashi, H. Sakaeb, K. Tatsumi, Z. Ogumi, Rock-salt-type lithium metal sulphides as novel positive-electrode materials. *Sci. Rep.* **4**, 4883 (2015).

30. A. Sakuda, K. Ohara, T. Kawaguchi, K. Fukuda, K. Nakanishi, H. Arai, Y. Uchimoto, T. Ohta, E. Matsubara, Z. Ogumi, K. Kuratani, H. Kobayashi, M. Shikano, T. Takeuchi, H. Sakaeb, A reversible rocksalt to amorphous phase transition involving anion redox. *Sci. Rep.* **8**, 15086 (2018).

31. J. K. Kim, A. Manthiram, A manganese oxyiodide cathode for rechargeable lithium batteries. *Nature* **390**, 265–267 (1997).

32. Y.-Y. Hu, Z. Liu, K.-W. Nam, O. J. Borkiewicz, J. Cheng, X. Hua, M. T. Dunstan, X. Yu, K. M. Wiaderek, L.-S. Du, K. W. Chapman, P. J. Chupas, X.-Q. Yang, C. P. Gley, Origin of additional capacities in metal oxide lithium-ion battery electrodes. *Nat. Mater.* **12**, 1130–1136 (2013).

33. G. Assat, A. Iadecola, C. Delacourt, R. Dedryvère, J.-M. Tarascon, Decoupling cationic–anionic redox processes in a model Li-rich cathode via *Operando* x-ray absorption spectroscopy. *Chem. Mater.* **29**, 9714–9724 (2017).

34. F. Jalilehvand, Sulfur: Nota “silent” element any more. *Chem. Soc. Rev.* **35**, 1256–1268 (2006).
35. M. Saubanère, M. Ben Yahia, S. Lebègue, M.-L. Doublet, An intuitive and efficient method for cell voltage prediction of lithium and sodium-ion batteries. *Nat. Commun.* **5**, 5559 (2014).

36. F. Izumi, K. Momma, Three-dimensional visualization in powder diffraction. *Solid State Phenom.* **130**, 15–20 (2007).

37. K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Cryst.* **44**, 1272–1276 (2011).

38. B. Yao, T. Sun, A. Warren, H. Heinrich, K. Barmak, K. R. Coffey, High contrast hollow-cone dark field transmission electron microscopy for nanocrystalline grain size quantification. *Micron* **41**, 177–182 (2010).

39. R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.* **A32**, 751–767 (1976).

40. B. Raguenet, G. Tricot, G. Silly, M. Ribes, A. Pradel, The mixed glass former effect in twin-roller quenched lithium borophosphate glasses. *Solid State Ion.* **208**, 25–30 (2012).