



Title	Two-Dimensional Hybrid Halide Perovskite as Electrode Materials for All-Solid-State Lithium Secondary Batteries Based on Sulfide Solid Electrolytes
Author(s)	Fujii, Yuta; Ramirez, Daniel; Rosero-Navarro, Nataly Carolina et al.
Citation	ACS applied energy materials, 2(9), 6569-6576 https://doi.org/10.1021/acsaem.9b01118
Issue Date	2019-09
Doc URL	https://hdl.handle.net/2115/79190
Rights	This document is the Accepted Manuscript version of a Published Work that appeared in final form in ACS applied energy materials, copyright c American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://pubs.acs.org/doi/10.1021/acsaem.9b01118 .
Type	journal article
File Information	ACS AppliedEnergyMaterias2019-acceptedversion.pdf



Two-dimensional hybrid halide perovskite as electrode materials for all-solid-state lithium secondary batteries based on sulfide solid electrolytes

*Yuta Fujii, ^a Daniel Ramirez, ^b Nataly Carolina Rosero-Navarro, ^{*c} Domingo Jullian, ^d Akira Miura, ^c Franklin Jaramillo, ^{*b} and Kiyoharu Tadanaga, ^c*

^a Graduate School of Chemical Sciences and Engineering, Hokkaido University, Sapporo 060-8628, Japan

^b Centro de Investigación, Innovación y Desarrollo de Materiales – CIDEMAT, Facultad de Ingeniería, Universidad de Antioquia UdeA, Calle 70 No. 52-21, Medellín 050010, Colombia

^c Division of Applied Chemistry, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

^d Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-8628, Japan

* Corresponding authors: F.J. franklin.jaramillo@udea.edu.co, NC.R.N. rosero@eng.hokudai.ac.jp

ABSTRACT

All-solid-state lithium secondary battery using two-dimensional hybrid halide perovskite (2D-HHP) $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$ as electrode materials and sulfide-based solid electrolyte is fabricated for the first time. Although large amounts of lithium-ion conductor have been mixed in the electrodes of the all-solid-state batteries based on sulfide solid electrolytes, the high lithium-ion coefficient of the 2D-HHP, around $10^{-7} \text{ cm}^2 \text{ s}^{-1}$, allowed the suitable operation of the batteries without the addition of any lithium-ion conductor into the electrode. The lithium-ion diffusion in the electrode improves with the temperature, showing a better performance at 100 °C and keeping a low resistance between electrode/electrolyte interface of 13 Ω . The all-solid-state battery retains a reversible capacity of more than 242 mAh g^{-1} for 30 cycles at 0.13 mA cm^{-2} with a negligible capacity fade. The mechanism of the lithium storage into the 2D-HHP electrode material consists of a three-step reaction: Li^+ insertion/extraction, conversion, and alloying–dealloying reactions.

Rechargeable lithium-ion secondary batteries are powerful energy storage systems used successfully in various electronic devices that are part of daily life. Currently, a commercialized lithium secondary battery consists of a lithium transition-metal oxide (e.g., LiCoO_2) as positive electrode, graphite as negative electrode and an organic electrolyte containing lithium salts embedded in a separator felt. The ever-growing demand for higher energy and power densities for large scale energy storage such as is the case of the electric vehicles; has motivated the development of new alternative technologies and the improvement of the electrochemical properties of the materials that are part of the battery. Particularly, the use of flammable organic liquid electrolytes restricts the operating limits of the battery in terms of electrochemical potential windows and temperature with the risk of undesired reactions and leak-out, leading to fire or explosion.

The all-solid-state lithium secondary batteries have been proposed as safe next-generation electrochemical storage. Recently, novel sulfide solid electrolytes with high ionic conductivity of $10^{-2} \text{ S cm}^{-1}$, comparable to conventional liquid electrolytes, have been reported.^{1,2} The sulfide solid electrolytes show not only high conductivity but also, a wide electrochemical potential window and high chemical stability at low and high temperatures.³⁻⁶ In addition, the excellent mechanical strength/flexibility of the sulfide solid electrolyte facilitates the formation of low interfacial resistance between electrode and electrolyte by a simple cold-pressure procedure.^{3,5,6,7,8} The fabrication of all-solid-state batteries based on sulfide solid electrolytes requires composite electrodes consisting of a mixture of active material, sulfide solid

electrolyte (around 30 to 60 wt%^{3,6}) and carbon additives to ensure ionic and electronic conduction paths to the active material. One of the current drawbacks is the large content of the sulfide solid electrolyte in the composite electrode, that restricts the energy density of the battery. For example, some electrode materials such as LiCoO₂, sulfur, Li₄Ti₅O₁₂, and graphite require the mixing with the solid electrolytes and carbon additives because of their insufficient ionic and electronic conducting properties.^{9–11} Thus, an ideal electrode material with an inherent sufficient ionic and electronic conducting properties is strongly desired. For example, FePS₃ can be used as an electrode without a solid electrolyte or conductor additive,¹² because the FePS₃ electrode has moderate electronic conductivity ($\sim 10^{-5}$ S cm⁻¹)¹³ as well as a layered structure, which is expected to lead to high ionic diffusion. Moreover, high temperature operation can easily enhance the ionic and electronic conducting properties of an electrode material. However, side reactions at high temperature that lead to the formation of an electrode/electrolyte interfacial layer with high resistance must be prevented.

HHPs are well known materials for their incredible optical properties, which make them very attractive for light emitting diodes^{14,15} and solar cells.^{16–18} Their potential as electrode materials has been recently explored,^{19–24} and the lithium storage mechanism by insertion/extraction, conversion, and alloying–dealloying has been proposed.²⁵ Their characteristic structure allows an efficient ionic diffusion (Li⁺, Na⁺). Actually, the coefficient of Li⁺ diffusion is as high as $\sim 10^{-7}$ cm² s⁻¹, implying that Li⁺ conductivity of lithiated HHP can reach $\sim 10^{-3}$ S cm⁻¹.²⁶ This

property makes them a potential alternative to be used as electrodes for all-solid-state batteries without the addition of any lithium-ion conductor.

Here, 2D-HHP with a structure of $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$ was evaluated as an electrode material for an all-solid-state battery based on a sulfide solid electrolyte at different temperatures. The synthesis of the 2D-HHP by solution-precipitation method is described at Supporting Information. 2D-HHP are obtained by the partial substitution of the A site cation in the three-dimensional (3D) ABX_3 perovskite. The resulting material is then referred as a Ruddlesden-Popper perovskite with lower dimensionality as the number of inorganic layers separated by the hydrophobic cation (n) goes from infinity to one,²⁷ and the chemical formula is $\text{A}'_2\text{A}_{n-1}\text{B}_n\text{X}_{3n+1}$ where A, A' are cations, B is metal and X is halide.

Figure 1 shows (a) SEM image and (b) enlarged SEM image of the prepared 2D-HHP. The particle size of the 2D-HHP is approximately ten micrometers. A sheet-like structure, in agreement with the 2D structure of the HHP, is observed, as indicated in Figure 1 (b). The constituent elements (C, N, Pb, and Br) of the 2D-HHP are distributed uniformly in nanoscale (STEM images shown in Figure S1 (a)–(e)). Figure 1 (c) shows the XRD pattern of the 2D-HHP before and after heating at 100 °C for several days. The low angle peaks corresponding to the reflection planes (040), (060) and (080) match well with the experimental and theoretical XRD patterns of the 2D-HHP previously reported.²¹ The additional peak around $2\theta = 9.8^\circ$ should correspond to a 2D perovskite with a different dimensionality, but still a 2D material. The crystal phase of the obtained perovskite did not change by heating at 100 °C for 14 days,

evidencing high chemical stability that could be useful for its application in batteries operated at extreme working conditions such as high temperatures.

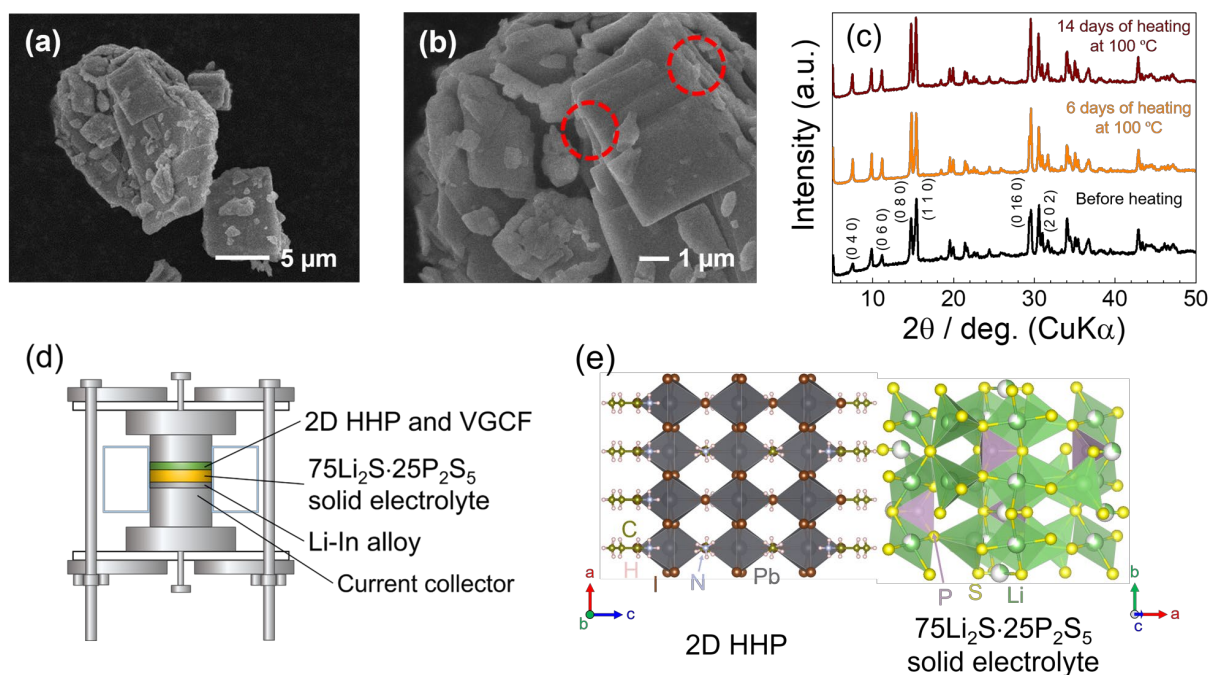


Figure 1. (a) SEM image and (b) enlarged SEM image of the prepared 2D-HHP ($(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$). Red dotted circles indicate the sheet-like structure. (c) XRD pattern of the 2D-HHP before and after heating at 100 °C for several days. (d) Schematic image of the all-solid-state battery using the 2D-HHP. (e) Schematic image of the 2D-HHP and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ ($\beta\text{-Li}_3\text{PS}_4$) solid electrolyte structures.^{21,26,27}

To fabricate the all-solid-state lithium battery and evaluate the 2D-HHP as an electrode material, the 2D-HHP was used as-synthesized powder without any further treatment. Figure 1 (d) illustrates a schematic image of the all-solid-state battery consisting of a three-layered pellet prepared by uniaxial pressing at room temperature.²⁸ A schematic image of the 2D-HHP and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ ($\beta\text{-Li}_3\text{PS}_4$) solid electrolyte structures also shown in Figure 1 (e).^{24,29,30} In the battery, the Li-In alloy layer works as a negative electrode and $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ (mol%) solid

electrolyte glass works as a separator layer. The third layer is a composite powder consisting of the 2D-HHP and vapor grown carbon fibers (VGCF), working as a positive electrode (see Supporting Information for further details). The carbon was added to the composite electrode to enhance the electronic conductivity.

Figure 2 shows discharge-charge curves of the all-solid-state batteries using the 2D-HHP at (a) 25 °C, (b) 60 °C, and (c) 100 °C. In Figure 2, (d) cycle ability, (e) coulomb efficiency and (f) capacity retention of the all-solid-state batteries with the 2D-HHP at the different temperatures are also shown. In the discharge-charge measurement, the cut-off voltage was set to -0.52 V vs. Li-In alloy for discharge and 2.58 V vs. Li-In alloy for charging. The current density was set to 0.13 mA cm^{-2} , and the batteries were firstly discharged (lithium insertion). The battery operated at 25 °C showed discharge-charge behavior, but the reversible capacity is only 12 mAh g^{-1} at the first cycle. The battery operated at 60 °C shows a higher reversible capacity of 93 mAh g^{-1} at the first cycle compared with the battery operated at 25 °C. From the second cycle onwards, the battery retains a discharge capacity of more than 46 mAh g^{-1} . At the higher temperature operation of 100 °C, the battery performance is further improved compared with those at 25 °C and 60 °C. The reversible capacity is increased to 249 mAh g^{-1} at the first cycle, and the discharge capacity is more than 242 mAh g^{-1} for 30 cycles even though the composite electrode did not contain solid electrolyte. The coulombic efficiency of the batteries is more than 90 % after initial cycles (~ 8 cycles) onwards (Figure 2 (e)), in the case of the battery operated at 100 °C after the initial third cycle. The large irreversible capacity observed

at the initial cycle is attributed to irreversible reactions between 2D-HHP electrode and solid electrolyte. The capacity retention (lithium extraction) of the battery operated at 25 °C and 60 °C shows a continuous capacity fade, while the battery operated at 100 °C displays a significant improvement in the lifetime of the battery achieving a capacity retention close to 100 % after 30 cycles. The clear temperature dependence of the battery performance of the 2D-HHP is attributed to a better lithium-ion diffusion in the 2D-HHP promoted by the heating of the battery. This behavior has also been observed in similar systems with others composite electrode not containing lithium (conversion materials).³¹ Li-ion batteries using LiCoO₂ have also shown a similar temperature dependence of the discharge behavior,³² in which faster lithium-ion diffusion into the LiCoO₂ structure is obtained at higher temperatures resulting in the better discharge performance. Thus, a temperature of 100 °C was high enough to promote a faster lithium-ion diffusion ($\sim 10^{-7} \text{ cm}^2 \text{ s}^{-1}$)²⁶ into 2D-HHP structure resulting in adequate and superior battery performance. Note that the operating temperature of the battery at 100 °C is expected not to cause huge negative effect on the 75Li₂S·25P₂S₅ solid electrolyte used as the separator layer because this temperature is low enough not to produce structural changes such as crystallization which have been reported to be in the range from 220 °C to 260 °C.³³ Moreover, the conductivity of the 75Li₂S·25P₂S₅ glass electrolyte at 100 °C is expected to be in the order of $10^{-3} \text{ S cm}^{-1}$ ($\sim 10^{-4} \text{ S cm}^{-1}$ at 25 °C) ensuing the lithium ionic conductivity during charge and discharge processes.^{33,34}

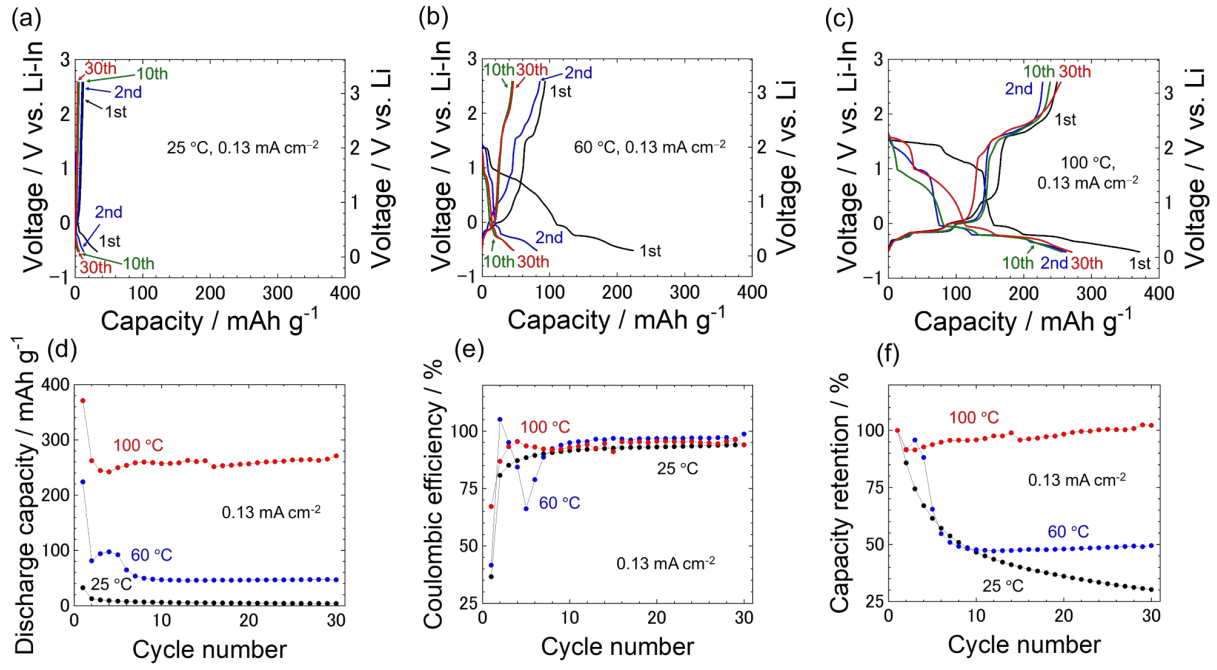


Figure 2. Discharge-charge curves of the all-solid-state batteries using the prepared 2D-HHP ($(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$) at (a) 25 °C, (b) 60 °C, and (c) 100 °C. (d) Cycle ability, (e) coulombic efficiency, and (f) capacity retention of the all-solid-state battery with the 2D-HHP at different temperature (25 °C, 60 °C, and 100 °C).

Figure 3 shows Nyquist plots of the all-solid-state battery with the 2D-HHP (a) before discharge and charge, and (d) after the 30th charge at 100 °C. The enlarged Nyquist plots are also included in Figure 3 (b–c, e–f) to differentiate the individual contributions at higher frequencies. In the Nyquist plots, three resistance components followed of the capacitive tail at low frequency (0.1 – 0.01 Hz) which is ascribed to electrodes impedance (Li-In alloy and electrode composite with current collectors of stainless steel) are confirmed. The resistive components were identified according to a previous report.^{3,35} The resistance (R_1) observed at high frequency (1 MHz), corresponding to the interception with the real axis, is attributed to the solid electrolyte separator layer. The resistance (R_2) at middle frequency (100 – 200 kHz),

shown as green semicircles in Figure 3 (c) and (f), correspond to the interfacial resistance between the 2D-HHP electrode and the $75\text{Li}_2\text{S}\cdot 25\text{P}_2\text{S}_5$ solid electrolyte. A resistance (R_3) at low frequency (50 – 500 Hz), shown as orange semicircles in Figure 3 (c) and (f), is attributed to the interface with Li-In alloy electrode. In order to assess to the value of each resistance, the impedance profiles were fitted to equivalent circuits illustrated in Figure 3 (g) and (h). The constant phase elements (CPE), CPE1 and CPE2, are used to simulate the capacitive behavior of R_2 and R_3 resistances, respectively. The Warburg element (W_o) and CPE3 were used to simulate the diffusive behavior at low frequency range. In the fitting of the impedance profile of the battery after the 30th charge at 100 °C (Figure 3 (h)), a constant phase element was used instead of a Warburg element to reduce the error since limited data at low frequency were obtained, even when the data were collected until 0.01 Hz. This behavior is attributed to the high resistance of the composite electrode (before charge-discharge) because of the deficiency of the charges in the 2D-HHP electrode, which is visibly reduced after the 30th charge where the lithium pathway to the inside of the electrode composite is expected. Table I shows resistance values extracted from the fitting results (solid red line in Figure 3).

After the 30th charge, the R_1 resistance increases from 7.5 Ω to 16.6 Ω . This suggests that the lithium-ion conductivity of the solid electrolyte decreases by extended heating at 100 °C but the solid electrolyte is relatively stable even at 100 °C. Actually, an all-solid-state battery using the $\text{Li}_2\text{S}\text{-P}_2\text{S}_5$ solid electrolyte system has been reported to show stable discharge-charge behavior at high temperature such as 120 °C.³¹ The R_2 resistance increases from 13.0 Ω to 33.7

Ω after the 30th charge, which corresponds to a slight increase of $\sim 20 \Omega$. This resistance, associated to the elemental diffusion at the electrode-electrolyte interface, is reported to achieve higher values up to $\sim 300 \Omega$ in an all-solid-state battery using LiCoO_2 electrode and $\text{Li}_2\text{S-P}_2\text{S}_5$ solid electrolyte.^{3,30} This suggests that a favorable interface can be formed in all-solid-state batteries using the 2D-HHP. The R_3 resistance is not changed significantly over cycling keeping a value around 50Ω .

It can be inferred that the interface formed between 2D-HHP electrode and sulfide solid electrolyte in the all-solid-state battery is electrochemically stable even at the high operating temperature of 100°C . Moreover, the high capacity retention of the all-solid-state battery using the 2D-HHP has not been observed in the Li-ion batteries prepared with the 2D or 3D hybrid perovskites and organic liquid electrolytes.^{19,36}

In addition, the interface between the solid electrolyte and 2D-HHP composite electrode, and 2D-HHP electrode after the 30th charge was evaluated by SEM-EDS analysis (Figure 4 (a–e)), where the composite electrode is observed to be sufficiently attached to the solid electrolyte layer without any evidence of an elemental diffusion, in good agreement with the low interfacial resistance (34Ω) of the all-solid-state battery determined by impedance analysis (Figure 3 d–f).

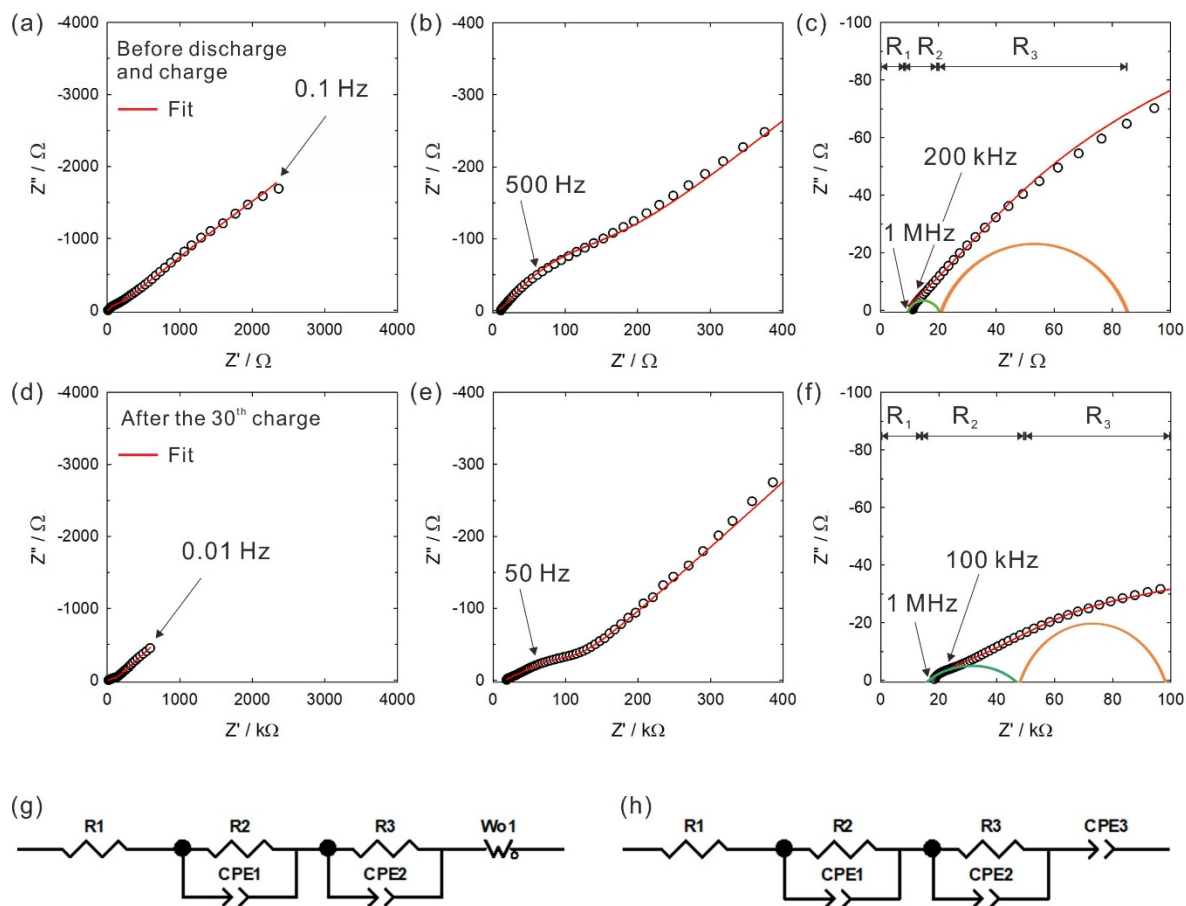


Figure 3. Nyquist plots of the all-solid-state battery with the 2D-HHP (a) before discharge and charge, and (d) after the 30th charge at 100 °C. These enlarged Nyquist plots (b–c) before discharge and charge, and (e–f) after the 30th charge are also shown. Equivalent Circuit models used to fit the impedance profiles of the all-solid-state battery with the 2D-HHP (g) before discharge and charge, and (h) after the 30th charge at 100 °C, respectively.

Table I. Fitting results of the impedance spectra of the all-solid-state battery with the 2D-HHP (a) before discharge and charge, and (d) after the 30th charge at 100 °C.

	R_1 / Ω	R_2 / Ω	R_3 / Ω
Before discharge and charge	7.5	13.0	56.9
After the 30th charge	16.6	33.7	49.6

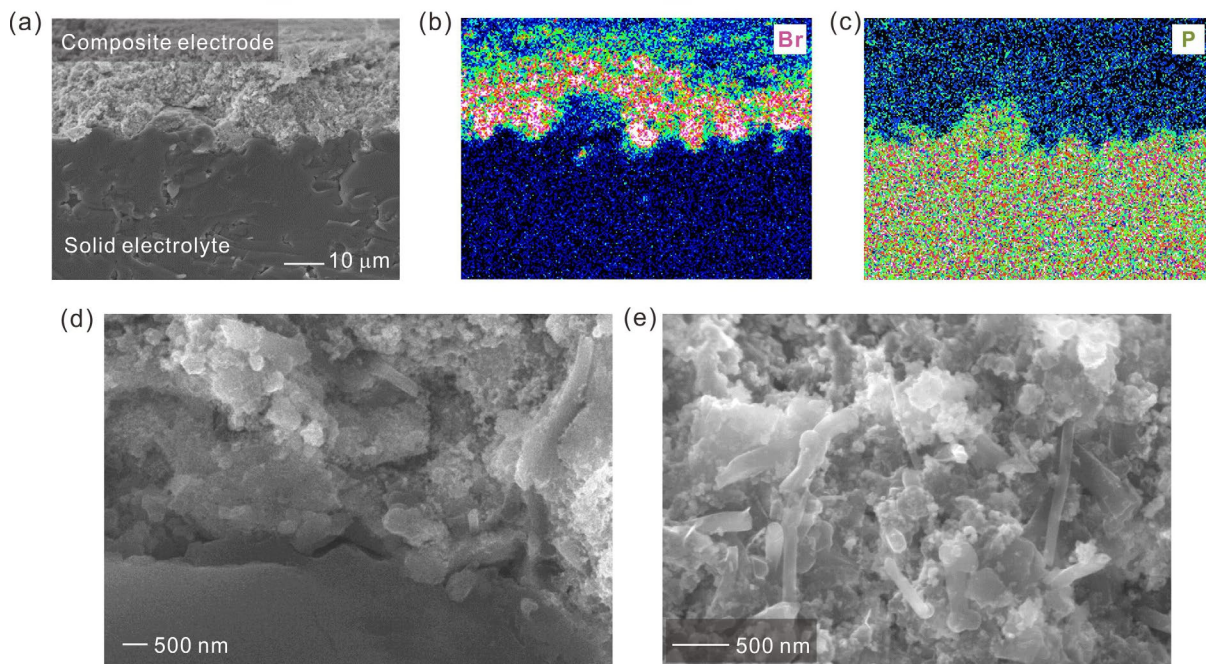
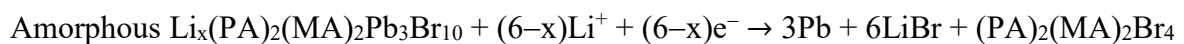


Figure 4. (a) Cross-sectional SEM image, and EDS mapping of (b) Br and (c) P of the electrode-electrolyte interface of the all-solid-state battery after the 30th charge. (d) SEM images details of the interface between 2D-HHP electrode and solid electrolyte and (e) 2D-HHP electrode.

To inquire about the mechanisms of lithium storage of the all-solid-state battery using the 2D-HHP material, a series of ex-situ XRD measurements at different stages of the discharge-charge processes were carried out. Figure 5 shows (a) the first discharge-charge curve of the all-solid-state battery using the 2D-HHP and (b) the XRD patterns of the composite electrodes at different voltage during the first discharge and first charge cycles. The colored circles in the discharge-charge curve indicate the measurement points of the XRD patterns (A) before discharge and charge, (B) at 1.43 V and (C) at 0 V vs. Li-In alloy during the first discharge process, (D) after the first discharge at -0.52 V vs. Li-In alloy, and (E) after the first charge at 2.58 V vs. Li-In alloy. To correct the XRD patterns, Si powders were used as a standard

material for the composite electrodes. In the XRD pattern at 1.43 V vs. Li-In alloy during the discharge process, the peaks due to Pb meal (31.2 and 36.2 °) and LiBr (28.0 and 32.5 °) were confirmed, and unknown peaks (22.0 and 38.7 °) were also observed. This result indicates that the conversion reaction can occur during the early stage of the discharge process (Figure 5 (a), between (A) and (B) points). It has been reported that batteries using CH₃NH₃PbBr₃, which is 3D-HHP, show the discharge plateau at ~2.3 V vs. Li, corresponding to ~1.7 V vs. Li-In alloy, through the formation of the Li⁺-inserted CH₃NH₃PbBr₃.²⁵ In case of the all-solid-state battery prepared with 2D-HHP, a similar discharge plateau was observed at ~1.5 V vs. Li-In alloy. In contrast, this discharge plateau was not observed in a lithium-ion battery using PbO, where only conversion and alloying–dealloying process has been reported.³⁷ Thus, conversion and Li⁺ insertion reactions in the 2D-HHP are expected to occur during the early stage of the discharge process. The possible Li⁺ insertion and conversion reactions are shown below:

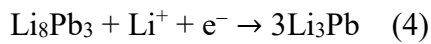
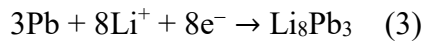


(2)

(where MA: CH₃NH₃, PA: CH₃(CH₂)₂NH₃)

In these reactions, Pb²⁺ can be reduced to Pb⁰. The unknown peaks would be attributed to an organic component such as (CH₃(CH₂)₂NH₃)₂(CH₃NH₃)₂Br₄. In XRD pattern (C) at 0 V vs. Li-In alloy during the discharge process, the peaks due to Pb meal and LiBr, and unknown peaks (22.0 and 38.7 °) were again observed, suggesting that the conversion reaction (equation (2))

proceeded in the discharge process between (B) at 1.43 and (C) at 0 V vs. Li-In alloy. In XRD pattern (D) after the discharge at -0.52 V vs. Li-In alloy, the peaks due to LiBr, Li_8Pb_3 (22.2, 24.2, 25.0, 29.1, and 37.7°), and Li_3Pb (23.0, 26.6, and 38.0°), and unknown peaks (22.0, 31.3, and 38.7°) were confirmed. This result indicates that the alloying reactions occurs during last stage of the discharge process (Figure 5 (a), between (C) and (D)), as shown below:



The unknown peak at 31.3° would be attributed to the Li-Pb alloy component. The XRD pattern (E) after the first charge shows almost the same diffraction peaks that those observed in XRD patterns of (B) at 1.43 V and (C) at 0 V vs. Li-In alloy during the discharge process. Thus, the dealloying reactions occur during the charge process. In the charge cycle, the plateau was observed at ~ 1.7 V vs. Li-In alloy. Considering the discharge plateau observed at ~ 1.5 V vs. Li-In alloy in the first discharge cycle, which can correspond to the Li^+ insertion reaction, this charge plateau can be attributed to the Li^+ extraction reaction from the Li^+ -inserted 2D-HHP. Since the peaks due to the 2D-HHP are not detected after the charge cycle, 2D-HHP with amorphous feature may be formed in the Li^+ extraction reaction. Therefore, not only the dealloying but also the Li^+ extraction reactions may occur during the charge cycle.

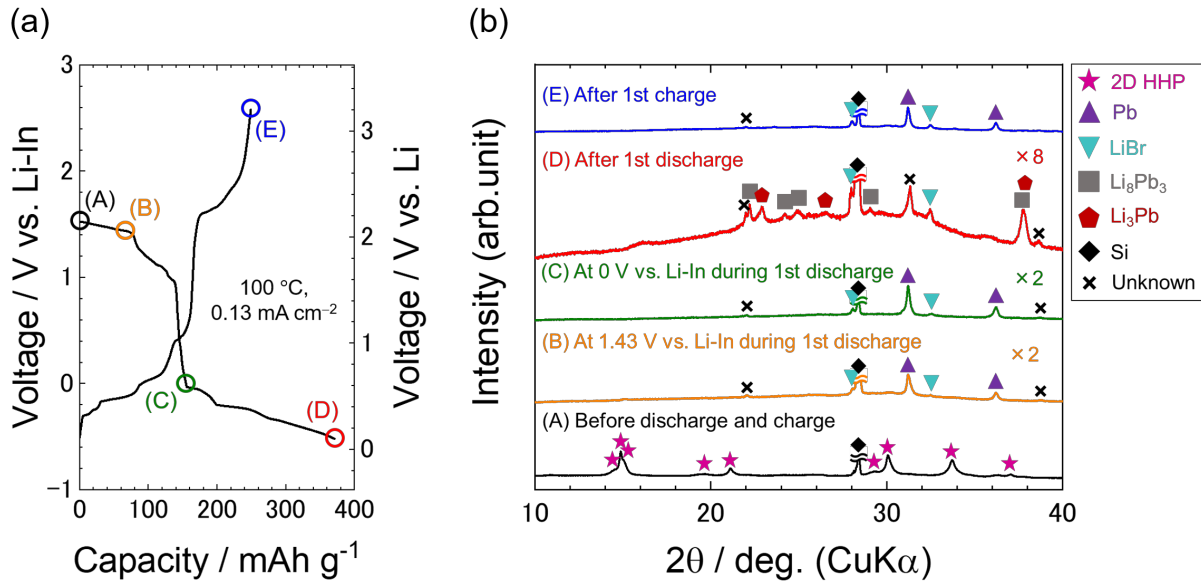
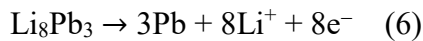
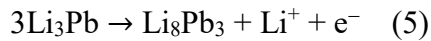


Figure 5. (a) First discharge-charge curve of the all-solid-state battery using the 2D-HHP and (b) XRD patterns of the composite electrodes at different voltage during the first discharge and first charge processes. The colored circles in the discharge-charge curve indicates the measurement points of the XRD patterns (A) before discharge and charge, (B) at 1.43 and (C) at 0 V vs. Li-In alloy during the discharge process, (D) after the first discharge at -0.52 V vs. Li-In alloy, and (E) after the first charge at 2.58 V vs. Li-In alloy. To correct XRD patterns, Si powders as standard material were mixed into the composite electrodes.

The first charge reactions are shown in below:



(MA: CH_3NH_3 , PA: $\text{CH}_3(\text{CH}_2)_2\text{NH}_3$)

Thus, the mechanism of the lithium storage into the 2D-HHP electrode material consists of a three-step reaction: Li^+ insertion/extraction, conversion, and alloying–dealloying reactions.

The favorable electrochemical performance of the battery can be attributed to both the high

lithium-ion diffusion of the 2D-HHP structure facilitated at high temperatures and the formation of LiBr during the initial discharge-charge processes. LiBr, known as additives to increase Li^+ conductivity of polymers and glasses, can enhance the lithium pathway into composite electrode.

Finally, the 2D-HHP electrode material can be more effective than other inorganic materials based on Pb or their mixture with additives such as LiBr because the organic component in the unique 2D-HHP structure (organic cation: $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2^{4+}$) is expected to prevent or minimize the large volume change of the electrode during the discharge-charge processes (lithium insertion/disinsertion) which coincide with the observed electrochemical behavior of the all-solid-state battery where a negligible capacity degradation after the second cycle was obtained. It is anticipated that the chemical structure of the 2D-HHP material strongly affects the interfacial reactions with the solid electrolyte and therefore, the electrochemical performance of the battery is expected to be improved by the change in the structure of the metal halide perovskite such as the use of Sn or Ni instead of Pb, Cl instead of Br and the volume of organic cation, etc.

Conclusions

All-solid-state lithium secondary battery using 2D-HHP $(\text{CH}_3(\text{CH}_2)_2\text{NH}_3)_2(\text{CH}_3\text{NH}_3)_2\text{Pb}_3\text{Br}_{10}$ (electrode material) sulfide solid electrolyte (separator layer) and Li-In alloy (negative electrode) was successfully prepared and evaluated at different temperatures from 25 °C to 100

°C in a potential range between –0.52 V to 2.58 V vs. Li-In alloy. In the higher temperature operation at 100 °C, the all-solid-state battery performance was further improved compared with those at 25 °C and 60 °C because of a faster lithium-ion diffusion ($\sim 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) into 2D-HHP structure and its high chemical stability verified by XRD measurement. The all-solid-state battery operated at 100 °C achieved a high reversible capacity of more than 242 mAh g⁻¹ for 30 cycles at 0.13 mA cm⁻², even though the absence of lithium-ion conductor additives in the composite electrode. Moreover, a low interfacial resistance between 2D-HHP and sulfide solid electrolyte of only 34 Ω after 30 cycles was determined, which shows the high electrochemical stability of the battery. The mechanism of the lithium storage into the 2D-HHP electrode material was investigated by ex-situ XRD measurements of composite electrode at different stages of the discharge-charge processes. The results suggest that the lithium storage of the battery consists of a three-step reaction: Li⁺ insertion/extraction, conversion, and alloying–dealloying reactions.

Acknowledgements

This work was partially supported by Grant-in-Aid for JSPS Research Fellow (18J11169). D.R. and F.J. acknowledge to *Universidad de Antioquia* for the project support 2018-19971. The SEM-EDS analysis was carried out with JIB4600F at the “Joint-use Facilities: Laboratory of Nano-Micro Material Analysis”, Hokkaido University, supported by “Material Analysis and Structure Analysis Open Unit (MASAOU)”.

References

1. Cao, C.; Li, Z.; Wang, X.-L.; Zhao, X.; Han, W.-Q., Recent advances in inorganic solid electrolytes for lithium batteries. *Frontiers in Energy Research* **2014**, *2*.
2. Manthiram, A.; Yu, X.; Wang, S., Lithium battery chemistries enabled by solid-state electrolytes. *Nature Reviews Materials* **2017**, *2*, 16103.
3. Sakuda, A.; Hayashi, A.; Tatsumisago, M., Interfacial Observation between LiCoO₂ Electrode and Li₂S–P₂S₅ Solid Electrolytes of All-Solid-State Lithium Secondary Batteries Using Transmission Electron Microscopy. *Chemistry of Materials* **2010**, *22* (3), 949-956.
4. Rangasamy, E.; Liu, Z. C.; Gobet, M.; Pilar, K.; Sahu, G.; Zhou, W.; Wu, H.; Greenbaum, S.; Liang, C. D., An iodide-based Li₇P₂S₈I superionic conductor. *J. Am. Chem. Soc.* **2015**, *137* (4), 1384-1387.
5. Kato, Y.; Hori, S.; Saito, T.; Suzuki, K.; Hirayama, M.; Mitsui, A.; Yonemura, M.; Iba, H.; Kanno, R., High-power all-solid-state batteries using sulfide superionic conductors. *Nat. Energy* **2016**, *1*, 16030.
6. Hayashi, A.; Sakuda, A.; Tatsumisago, M., Development of Sulfide Solid Electrolytes and Interface Formation Processes for Bulk-Type All-Solid-State Li and Na Batteries. *Frontiers in Energy Research* **2016**, *4*.
7. Bucci, G.; Swamy, T.; Chiang, Y. M.; Carter, W. C., Modeling of internal mechanical failure of all-solidstate batteries during electrochemical cycling, and implications for battery design. *J. Mater. Chem. A* **2017**, *5* (36), 19422-19430
8. Miura, A.; Rosero-Navarro, N.C.; Sakuda, A.; Tadanaga, K.; Phuc, N.H.H.; Matsuda, A.; Machida, N.; Hayashi, A.; Tatsumisago, M., Liquid-phase syntheses of sulfide electrolytes for all-solid-state lithium battery. *Nature Reviews Chemistry* **2018**, *3*, 189-193.
9. Tatsumisago, M.; Nagao, M.; Hayashi, A. Recent development of sulfide solid electrolytes and interfacial modification for all-solid-state rechargeable lithium batteries. *Journal of Asian Ceramic Societies* **2013**, *1* (1), 17-25.
10. Sun, C.; Liu, J.; Gong, Y.; Wilkinson, D. P.; Zhang, J. Recent Advances in All-Solid-State Rechargeable Lithium Batteries. *Nano Energy* **2017**, *33*, 363-386.
11. Yue, J.; Yan, M.; Yin, Y. X.; Guo, Y. G. Progress of the Interface Design in All-Solid-State Li–S Batteries, *Advanced Functional Materials* **2018**, *28*, 1707533.
12. Fujii, Y.; Miura, A. Rosero-Navvaro, N. C.; Higuchi, M.; Kiyoharu, T., FePS₃ electrodes in all-solid-state lithium secondary batteries using sulfide-based solid electrolytes. *Electrochim. Acta* **2017**, *241*, 370-374.
13. Ichimura, K.; Sano, M., Electrical conductivity of layered transition-metal phosphorus trisulfide crystals. *Synthetic Metals* **1991**, *45* (2), 203-2111.
14. Lin, H.; Zhou, C.; Tian, Y.; Siegrist, T.; Ma, B., Low-Dimensional Organometal Halide Perovskites. *ACS Energy Letters* **2018**, *3* (1), 54-62.
15. Ban, M.; Zou, Y.; Rivett, J. P. H.; Yang, Y.; Thomas, T. H.; Tan, Y.; Song, T.; Gao, X.; Credington, D.; Deschler, F.; Sirringhaus, H.; Sun, B., Solution-processed perovskite light emitting diodes with efficiency exceeding 15% through additive-controlled nanostructure tailoring. *Nature Communications* **2018**, *9* (1), 1-10.
16. Yan, J.; Qiu, W.; Wu, G.; Heremans, P.; Chen, H., Recent progress in 2D/quasi-2D layered metal halide perovskites for solar cells. *Journal of Materials Chemistry A* **2018**, *6* (24), 11063-11077.
17. Fu, W.; Wang, J.; Zuo, L.; Gao, K.; Liu, F.; Ginger, D. S.; Jen, A. K. Y., Two-Dimensional Perovskite Solar Cells with 14.1% Power Conversion Efficiency and 0.68% External Radiative Efficiency. *ACS Energy Letters* **2018**, *3* (9), 2086-2093.

18. Ramirez, D.; Schutt, K.; Wang, Z.; Pearson, A. J.; Ruggeri, E.; Snaith, H. J.; Stranks, S. D.; Jaramillo, F., Layered Mixed Tin-Lead Hybrid Perovskite Solar Cells with High Stability. *ACS Energy Letters* **2018**, 3 (9), 2246-2251.
19. Xia, H.-R.; Sun, W.-T.; Peng, L.-M., Hydrothermal synthesis of organometal halide perovskites for Li-ion batteries. *Chem. Commun.* **2015**, 51 (72), 13787-13790.
20. Vicente, N.; Garcia-Belmonte, G., Methylammonium Lead Bromide Perovskite Battery Anodes Reversibly Host High Li-Ion Concentrations. *The Journal of Physical Chemistry Letters* **2017**, 8 (7), 1371-1374.
21. Tathavadekar, M.; Krishnamurthy, S.; Banerjee, A.; Nagane, S.; Gawli, Y.; Suryawanshi, A.; Bhat, S.; Puthusseri, D.; Mohite, A. D.; Ogale, S., Low-dimensional hybrid perovskites as high performance anodes for alkali-ion batteries. *J. Mater. Chem. A* **2017**, 5 (35), 18634-18642.
22. Dawson, J. A.; Naylor, A. J.; Eames, C.; Roberts, M.; Zhang, W.; Snaith, H. J.; Bruce, P. G.; Islam, M. S., Mechanisms of Lithium Intercalation and Conversion Processes in Organic-Inorganic Halide Perovskites. *ACS Energy Letters* **2017**, 2 (8), 1818-1824.
23. Li, Z.; Xiao, C.; Yang, Y.; Harvey, S. P.; Kim, D. H.; Christians, J. A.; Yang, M.; Schulz, P.; Nanayakkara, S. U.; Jiang, C.-S.; Luther, J. M.; Berry, J. J.; Beard, M. C.; Al-Jassim, M. M.; Zhu, K., Extrinsic ion migration in perovskite solar cells. *Energy & Environmental Science* **2017**, 10 (5), 1234-1242.
24. Ramirez, D.; Suto, Y.; Rosero-Navarro, N. C.; Miura, A.; Tadanaga, K.; Jaramillo, F., Structural and Electrochemical Evaluation of Three- and Two-Dimensional Organohalide Perovskites and Their Influence on the Reversibility of Lithium Intercalation. *Inorg. Chem.* **2018**, 57 (7), 4181-4188.
25. Vicente, N.; Bresser, D.; Passerini, S.; Garcia-Belmonte, G., Probing the 3-step Lithium Storage Mechanism in $\text{CH}_3\text{NH}_3\text{PbBr}_3$ Perovskite Electrode by Operando-XRD Analysis. *ChemElectroChem* **2019**, 6, 456-460.
26. Vicente, N.; Garcia-Belmonte, G. Organohalide perovskites are fast ionic conductors. *Adv. Energy Mater.* **2017**, 7, 1700710.
27. Blancon, J. C.; Tsai, H.; Nie, W.; Stoumpos, C. C.; Pedesseau, L.; Katan, C.; Kepenekian, M.; Soe, C. M. M.; Appavoo, K.; Sfeir, M. Y.; et al. Extremely Efficient Internal Exciton Dissociation through Edge States in Layered 2D Perovskites. *Science* **2017**, 355, 1288-1291.
28. Tatsumisago, M.; Hayashi, A., 19 - Chalcogenide glasses as electrolytes for batteries. In *Chalcogenide Glasses*, Adam, J.-L.; Zhang, X., Eds. Woodhead Publishing: 2014; pp 632-654.
29. Homma, K.; Yonemura, M.; Kobayashi, T.; Nagao, M.; Hirayama, M.; Kanno, R. Crystal Structure and Phase Transitions of the Lithium Ionic Conductor Li_3PS_4 . *Solid State Ionics* **2011**, 182, 53-58.
30. Momma, K. & Izumi, F. VESTA: a three-dimensional visualization system for electronic and structural analysis. *J. Appl. Crystallogr.* 41, 653-658.
- 31 Nagao, M.; Kitaura, H.; Hayashi, A.; Tatsumisago, M. High Rate Performance, Wide Temperature Operation and Long Cyclability of All-Solid-State Rechargeable Lithium Batteries Using Mo-S Chevrel-Phase Compound. *Journal of The electrochemical Society* **2013**, 160 (6), 819-823.
32. Okubo, M.; Tanaka, Y.; Zhou, H.; Kudo, T.; Honma, I; Determination of Activation Ennergy for Li Ion Diffusioin in Electrodes. *J. Phys. Chem B* 2009, 113, 2840-2847.
33. Mizuno, F.; Hayashi, A.; Tadanaga, K.; Tatsumisago, M. High lithium ion conducting glass-ceramics in the system $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$. *Solid State Ionics* **2006**, 177, 2721-2725.

34. Tatsumisago, M.; Hama, S.; Hayashi, A.; Morimoto, H.; Minami, T. New lithium ion conducting glass-ceramics prepared from mechanochemical $\text{Li}_2\text{S-P}_2\text{S}_5$ glasses. *Solid State Ionics* **2002**, 154 (155), 635-640.
35. Ohta, N.; Takada, K.; Zhang, L.Q.; Ma, R.Z.; Osada, M.; Sasaki, T., Enhancement of the high-rate capability of solid-state lithium batteries by nanoscale interfacial modification. *Adv. Mater.* **2006**, 18, 2226-2229.
36. Hasan, M.; Venkatesan, S.; Lyashenko, D.; Slinker, J. D.; Zakhidov, A., Solvent Toolkit for Electrochemical Characterization of Hybrid Perovskite Films. *Anal. Chem.* **2017**, 89 (18), 9649-9653.
37. Martos, M.; Morales, J.; Sánchez, L., Lead-based systems as suitable anode materials for Li-ion batteries. *Electrochimica Acta* **2003**, 48 (6), 615-621.
39. Gupta, S.; Fatnaik, S.; Chaklanobis, S.; Shahi, K. Enhanced electrical transport LiBr-LiI mixed crystals and $\text{LiBr-Al}_2\text{O}_3$ composites. *Solid State Ionics* **1988**, 31, 5-8.