



(51) International Patent Classification:

C01D 15/00 (2006.01) H01M 10/0562 (2010.01)

(21) International Application Number:

PCT/US2020/028471

(22) International Filing Date:

16 April 2020 (16.04.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/835,173 17 April 2019 (17.04.2019) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

(54) Title: METHOD FOR WET CHEMICAL SYNTHESIS OF LITHIUM ARGYRODITES

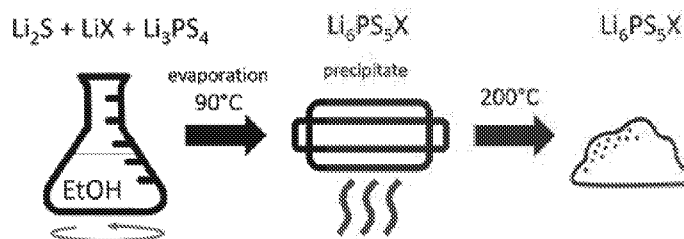


Figure 16

(57) Abstract: Methods for wet chemical synthesis of lithium argyrodites are provided, which in some embodiments include dissolving a stoichiometric mixture of precursors in a small quantity of solvent in an argon atmosphere, drying the mixture under vacuum or an inert gas atmosphere to evaporate the solvent, and then annealing to obtain a final lithium argyrodite product. Further embodiments comprise synthesizing the precursors, and excess halide doping to achieve higher ionic conductivity.



Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

METHOD FOR WET CHEMICAL SYNTHESIS OF LITHIUM ARGYRODITES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This international patent application claims the benefit of and priority to U.S. Provisional Patent Application serial number 62/835,173, with a filing date of 17 April 2019, the contents of which are fully incorporated herein by reference.

STATEMENT OF GOVERNMENT RIGHTS

[0002] This invention was made with United States Government support under Grant No. 1355438 awarded by the National Science Foundation. The United States Government has certain rights in the invention.

FIELD OF INVENTION

[0003] The embodiments described herein include methods for rapidly and economically synthesizing solid electrolytes for use in battery systems, further embodiments relate to wet chemical synthesis of lithium argyrodites and the use of halide doping.

BACKGROUND

[0004] The rapidly growing electric vehicle industry has spurred a strong need for the development of safer and higher energy density portable energy storage. Currently, conventional liquid electrolyte batteries, such as lithium ion, are in use for such applications. However, conventional liquid electrolyte batteries have limited energy density and thus limited energy capacity. In addition, conventional liquid electrolyte batteries are highly flammable and unstable. As a result, conventional liquid electrolyte batteries present a significant safety hazard, especially to the electric vehicle industry. Furthermore, conventional liquid electrolyte batteries often decompose at high voltages, which limit the use of high voltage cathode materials, and they often pose a risk of leakage.

[0005] All-solid-state batteries (ASSBs), on the other hand, have shown promise as next-generation lithium battery systems that address many of the drawbacks of the conventional liquid electrolyte batteries. ASSBs are promising candidates for the battery storage industry and are expected to improve safety, increase energy density, and enhance stability and durability. ASSBs comprise solid electrodes and solid electrolytes, instead of the liquid or polymer electrolytes found in the typical lithium ion battery. The solid electrolyte is an important component of ASSBs for its role in transporting the lithium ions and separating the anode from the cathode. Common inorganic solid electrolytes include oxides (e.g., garnet, perovskite), phosphates (e.g., LiPON, LATP, LAGP) and sulfides (e.g., $\text{Li}_2\text{S-P}_2\text{S}_5$, Li_3PS_4 , $\text{Li}_7\text{P}_3\text{S}_{11}$, Li_7PS_6). Among these, sulfide solid electrolytes have garnered significant attention due to their superior lithium ion conductivities, wide electrochemical window, thermal stability, and favorable mechanical properties such as easy densification and elastic modulus. Other desirable properties for a solid electrolyte include an ionic conductivity above 10^{-4} Siemens per centimeter (S cm^{-1}) at room temperature, a large electrochemical stability window, and stability against electrodes, especially a metallic lithium anode. In addition, the production cost is an important factor in the large-scale development of solid electrolyte materials.

[0006] Lithium argyrodites are a new and promising class of solid electrolyte sulfide-based lithium ion superconductors. Lithium argyrodites originate from the silver germanium sulfide mineral with the formula Ag_8GeS_6 , which is characterized by its high ionic conductivity ($\sim 10^{-3} \text{ S cm}^{-1}$) and fast silver ion (Ag^+) mobility. Pure lithium argyrodite (Li_7PS_6) is reported to have a cubic phase at high-temperature (HT) or an orthorhombic phase at low-temperature (LT). In particular, the cubic HT-phase shows higher ionic conductivities ($0.7\text{-}1.0 \times 10^{-3} \text{ S cm}^{-1}$) and can be stabilized by the replacement of the sulfur by halogen anions, such as chlorine, bromine, and iodine. Such lithium argyrodites are expressed by the formula $\text{Li}_m\text{PS}_n\text{X}_o$, where

X is either chlorine, bromine, or iodine. Lithium argyrodites without a halide are expressed by the formula Li_mPS_n .

[0007] Recent studies of lithium argyrodite materials have yielded a basic understanding of the temperature-dependent diffusion paths of ions based on their structural properties. In addition, strong interest has grown in the use of lithium argyrodites as solid electrolytes for ASSBs because of its (1) high intrinsic lithium-ion conductivities (10^{-2} to 10^{-3} S cm^{-1}), (2) impressive stability within a large electrochemical window (up to 7V, which is suitable even for high voltage cathode materials), and (3) composition flexibility (due to flexibility in both anion and cation doping).

[0008] Despite these important findings, however, the large-scale manufacturing of lithium argyrodites has not been achieved due to the harsh conditions required by the conventional synthesis methods: melt-quenching or high-energy ball milling. With these conventional approaches, Li_7PS_6 (as one example) has been synthesized through the solid-state reaction of Li_2S with P_2S_5 at 550 °C for several hours or even days. Moreover, the preparation conditions for melt-quenching are very difficult and harsh. For example, melt-quenching requires the careful and precise control of reactant concentrations, otherwise it results in impurities during the cooling process. Consequently, the industrial applicability and feasibility of the conventional melt-quenching synthesis method has shown limited to unlikely prospects. High-energy ball milling fabrication is also time consuming and it is difficult to obtain uniform products. For example, some conventional ball-milling methods require at least 5 hours and up to 4 days to complete (without accounting for the time required to complete full crystallization). For the entire crystallization process to be completed after the heating and cooling cycle, the conventional ball-milling method can take an additional 5 hours and up to 7 days.

[0009] Recently, wet chemical synthesis has attracted interest as an alternative to the conventional synthesis methods because of its flexibility for material preparation and manufacturing simplicity. However, the conventional wet chemical synthesis methods require expensive solvents such as tetrahydrofuran (THF), acetonitrile (ACN), and dimethoxyethane (DME). For the large-scale synthesis of lithium argyrodites, which is required for the development of ASSBs in next generation energy storage systems, lesser amounts of solvents, as well as inexpensive and less toxic would be preferred. Moreover, liquid synthesis for producing lithium argyrodites is always challenging due to the stability of precursors in a solvent; for example, P_2S_5 reacts with the ethanol to form dialkyl dithiophosphoric acid.

[0010] In addition, non-toxic solvent based liquid synthesis would be a more efficient and environmentally friendly approach to prepare homogenous composite cathodes for ASSBs. Typically, cathode materials have poor conductivities and require mixing with carbon/solid electrolyte to enhance their electronic/ionic conductivities. For example, melt-quenching and high-energy ball milling typically results in the aggregation of each component, and such fouling limits the efficiency and life cycle duration of electrodes used in synthesis of lithium argyrodites.

[0011] Furthermore, the conventional solid-state synthesis methods have not explored the impact of halide doping content on the structure and conductive properties of produced lithium argyrodite. This limitation may be due to the difficulty in introducing additional halide(s) into a lithium argyrodite structure utilizing the traditional solid-state synthesis methods because of the slow atom diffusion and lattice reorganization.

[0012] Accordingly, there is a significant need for more optimal solid electrolyte synthetic methods capable of producing lithium argyrodites on the commercial scale, i.e. kgs or higher. There is also a significant need for a synthetic method that is simpler, more efficient, requires shorter preparation times, results in more homogenous products with higher conductivities, and

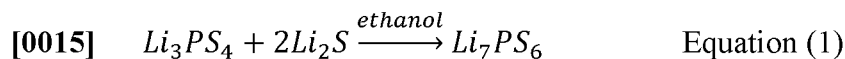
utilizes more environmentally friendly and affordable solvents. Such improvements would allow for the success of ASSBs at scales large enough to serve the mobile electric market. Along with other features and advantages outlined herein, the methods described herein according to multiple embodiments and alternatives meet these and other needs. In doing so, the methods described herein further advance the use of Li-ion conducting argyrodites in ASSBs by producing improved halide doped materials.

SUMMARY OF EMBODIMENTS

[0013] Multiple embodiments and alternatives are disclosed herein for the liquid synthesis of lithium argyrodites using precursors and inexpensive and nontoxic ethanol (EtOH) solvent. Although EtOH is preferred, other solvents also can be used within the scope of present embodiments, which provide for, without limitation, a method for rapid synthesis of lithium argyrodites in about 2 hours and at low sintering temperatures (e.g. 150°C). According to multiple embodiments and alternatives, structural and morphological investigations have determined that the synthesized lithium argyrodites have high phase purity, improved ionic conductivity at room temperature, high stability, and homogeneity. In some embodiments, halide doping occurs during the synthesis process to achieve higher ionic conductivity.

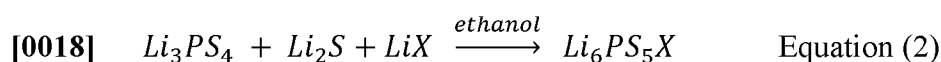
[0014] In some embodiments, the electrolyte Li_7PS_6 is synthesized by dissolving the precursors Li_2S and $\beta\text{-Li}_3\text{PS}_4$ in a small quantity of anhydrous ethanol (e.g. 25 ml) in argon atmosphere. Next, in some embodiments the mixture is dried above room temperature (e.g. greater than 22°C) under vacuum to evaporate the solvent yielding a white precipitate (not longer than 1 hour, preferably 40-50 minutes), and then treated above 150°C for 1 hour to obtain the final product (Li_7PS_6). In some embodiments, establishing a negative pressure of $10^{-2} \sim 10^{-3}$ mbar or lower provides efficient evaporation. In some embodiments, instead of a vacuum, the mixture is dried above room temperature in an inert gas atmosphere until a dry

powder is obtained. In the synthesis of Li_7PS_6 noted above, the chemical reaction of $\beta\text{-Li}_3\text{PS}_4$ and Li_2S is:



[0016] The Li_7PS_6 product synthesized according to multiple embodiments and alternatives exhibits high phase purity, favorable ionic conductivity, and significant electrochemical stability with metallic lithium anode. In some embodiments, methods for wet chemical synthesis provided herein utilize the economic and nontoxic ethanol solvent to synthesize lithium argyrodite solid electrolyte in significantly shorter time than conventional approaches.

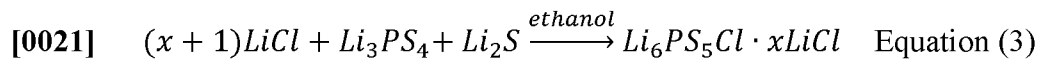
[0017] Present embodiments include those wherein steps include synthesis of electrolytes $\text{Li}_6\text{PS}_5\text{X}$ (where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$) by dissolving a stoichiometric mixture of Li_2S , Li_3PS_4 in acetonitrile (i.e., $(\text{ACN})_2$ in this exemplary statement)) and LiX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in a small quantity of anhydrous ethanol (25 ml) in argon atmosphere. In an exemplary embodiment, the $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ precursor is used (or pure Li_3PS_4 , or $\text{Li}_3\text{PS}_4 \cdot (\text{THF})$), then the solvent is evaporated above room temperature (e.g. more than 22°C) under vacuum (not longer than 1 hour, preferably 40-50 minutes), and the precipitate then is treated with heat (above 150°C for 1 hour) until the final product is synthesized (e.g. $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{Br}$, and $\text{Li}_6\text{PS}_5\text{I}$). The chemical reaction is:



[0019] Structural and morphological investigations revealed the final product exhibits high phase purity, high ionic conductivity at room temperature, and good stability with metallic lithium without evidence of side reactions.

[0020] In some embodiments according to the present disclosure, $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$) materials were synthesized by stoichiometrically tuning an excess amount of LiCl as the precursor. According to multiple embodiments and alternatives, the synthesized product has a molar ratio of sulfur to chloride in the range of 1.5:1 to 5.1. In some embodiments, the

synthesized product has a molar ratio of sulfur to chloride in the range of 2.5:1 to 5:1. An exemplary process includes first dissolving Li_2S and LiCl in ethanol, followed by the addition of Li_3PS_4 . Next, the mixture is stirred for 0.5 hours, dried above room temperature (e.g. 90°C as a non-limiting example) under vacuum to evaporate the ethanol, and then annealed above 150°C . As desired, chlorine content in $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$) is tuned by controlling the amount of LiCl precursor. In some embodiments, the following ratios of $\text{LiCl}:\text{Li}_3\text{PS}_4$ were controlled at 1:1, 1.5:1, 2:1, 2.5:1, and 3:1 to obtain the samples of $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{Cl} \cdot 0.5\text{LiCl}$ (i.e. $\text{Li}_{6.5}\text{PS}_5\text{Cl}_{1.5}$), $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ (i.e. $\text{Li}_7\text{PS}_5\text{Cl}_2$), $\text{Li}_6\text{PS}_5\text{Cl} \cdot 1.5\text{LiCl}$ (i.e. $\text{Li}_{7.5}\text{PS}_5\text{Cl}_{2.5}$) and $\text{Li}_6\text{PS}_5\text{Cl} \cdot 2\text{LiCl}$ (i.e. $\text{Li}_8\text{PS}_5\text{Cl}_3$), respectively. To investigate the annealing effect, $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ sample was heated at different temperatures (350°C , 550°C as non-limiting examples) for 6 hours under an Argon environment, according to multiple embodiments and alternatives. Herein, the annealed samples are referred to as $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ -350 and $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ -550, respectfully. The chemical reaction is represented by:



[0022] Advantageously, it has been discovered that when the Cl doping ratio is 2:1 (versus Li_3PS_4), the synthesized lithium argyrodite solid electrolyte exhibits a higher ionic conductivity of $4.4 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature when compared to other Cl doping ratios studied. The inventors are unaware of any reported conductivity value higher than this for an argyrodite prepared via liquid synthesis. In addition, the synthesized lithium argyrodite exhibits stability against a metallic lithium anode and lower activation energy.

[0023] The liquid synthesis method according to multiple embodiments and alternatives opens new possibilities for the success of ASSBs by generating lithium argyrodites with higher purity and more homogenous material through a simpler and scalable manufacturing process.

BRIEF DESCRIPTION OF THE FIGURES

[0024] The drawings and embodiments described herein are illustrative of multiple alternative structures, aspects, and features of the multiple embodiments and alternatives disclosed herein, and they are not to be understood as limiting the scope of any of these embodiments and alternatives. It will be further understood that the drawing figures described and provided herein are not to scale, and that the embodiments are not limited to the precise arrangements and instrumentalities shown.

[0025] Fig. 1 is a flow chart showing the steps of a method for wet chemical synthesis of lithium argyrodites

[0026] Fig. 2 shows a comparison of x-ray diffraction patterns (XRD) of Li_7PS_6 crystalline and $\beta\text{-Li}_3\text{PS}_4$ phase [panel (a)], and Raman spectra of Li_7PS_6 and $\beta\text{-Li}_3\text{PS}_4$ [panel (b)].

[0027] Fig. 3 shows scanning electron microscope (SEM) images of SEM images of the final Li_7PS_6 product [panel (a)] and Li_3PS_4 precursor [panel (b)].

[0028] Fig. 4 shows energy-dispersive X-ray spectroscopy (EDX) maps of Li_3PS_4 precursor prepared from ACN solution, wherein [panel (a)] shows the distribution of P atoms and [panel (b)] shows the distribution of S atoms. Fig. 4 also shows EDX maps of the final Li_7PS_6 product prepared from ethanol solution, wherein [panel (c)] shows the distribution of P atoms and [panel (d)] shows the distribution of S atoms.

[0029] Fig. 5 shows Arrhenius plots of Li_7PS_6 from ethanol and $\beta\text{-Li}_3\text{PS}_4$ from ACN [panel (a)], and comparison of conductivity values and synthesis time of Li_7PS_6 prepared by different methods [panel (b)].

[0030] Fig. 6 shows cyclic voltammetry curves of Li_7PS_6 and $\beta\text{-Li}_3\text{PS}_4$ solid electrolytes with metallic Li anode with Li/SE/Pt cell (scanning rate at 50 mV s^{-1} between -0.5 and 5 V vs. Li/Li^+ at room temperature) [panel (a)], and cycling performance of Li/ Li_7PS_6 /Li symmetric cell (current density of $50 \mu\text{A cm}^{-2}$) [panel (b)].

[0031] Fig. 7 is a flow chart illustrating the steps of a method for wet chemical synthesis of lithium argyrodites.

[0032] Fig. 8 shows XRD patterns of Li_7PS_6 solid electrolyte using different precursors: $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ complex and Li_3PS_4 .

[0033] Fig. 9 shows XRD patterns of Li_7PS_6 obtained from ethanol evaporation and dried at 90 °C.

[0034] Fig. 10 shows XRD patterns of $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ fresh precipitate and after 80 °C heat treatment, and $\beta\text{-Li}_3\text{PS}_4$ phase above 150°C annealing.

[0035] Fig. 11 shows XRD patterns of re-precipitated Li_3PS_4 material from ethanol dried at 80 °C and heated above 150°C, as well as reference patterns for Li_3PS_4 and $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$.

[0036] Fig. 12 shows Raman spectra of Li_3PS_4 , Li_3PS_4 re-precipitated from EtOH, and Li_7PS_6 prepared from Li_3PS_4 and Li_2S in EtOH medium.

[0037] Fig. 13 shows SEM images of the re-precipitated Li_3PS_4 sample from ethanol, wherein [panel (a)] has 5 μm scale and [panel (b)] has a 2 μm scale.

[0038] Fig. 14 shows Nyquist plots of synthesized Li_7PS_6 and $\beta\text{-Li}_3\text{PS}_4$ precursor, wherein the frequency range is from 1 MHz to 100 mHz.

[0039] Fig. 15 shows XRD patterns of Li_7PS_6 pellet after cycled in a symmetric cell ($\text{Li}/\text{Li}_7\text{PS}_6/\text{Li}$).

[0040] Fig. 16 is a flow chart showing the steps of a method for wet chemical synthesis of lithium argyrodites.

[0041] Fig. 17 shows XRD patterns of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{X}$ lithium argyrodites, wherein [panel (b)] is a close-up view of [panel (a)]. The dashed lines vertical lines in the bottom of [panel (a)] refer to standard diffraction peaks for $\text{Li}_6\text{PS}_5\text{X}$.

[0042] Fig. 18 shows Raman spectra of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{X}$ lithium argyrodites ($\text{X} = \text{Cl}$, Br , or I) from ethanol solution and Li_2S and P_2S_5 for comparison.

[0043] Fig. 19 shows SEM images of Li_7PS_6 [panel (a)] and $\text{Li}_6\text{PS}_5\text{X}$ products prepared from ethanol solution, where X is Cl [panel (b)], Br [panel (c)], and I [panel (d)].

[0044] Fig. 20 shows Arrhenius plots of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{X}$ lithium argyrodite samples from ethanol.

[0045] Fig. 21 panel shows cyclic voltammetry curves [panel (a)] of the liquid synthesized $\text{Li}_6\text{PS}_5\text{X}$ materials with metallic Li anode in the voltage window of 0.5-5.0 (vs Li/Li+) and the cycling performance of symmetric cells under a current density of 0.02 mA cm^{-2} [panel (b)].

[0046] Fig. 22 shows cycling of symmetric cells with Li/Li $_6\text{PS}_5\text{X}$ /Li structure, wherein [panel (b)] is a close-up view of a portion of [panel (a)].

[0047] Fig. 23 shows EDX maps of $\text{Li}_6\text{PS}_5\text{X}$ products (where X is Cl, Br and I) prepared from ethanol solution showing the distribution of S, P, and X atoms.

[0048] Fig. 24 shows multiple unit cell three-dimensional simulation of the crystal structure of certain $\text{Li}_6\text{PS}_5\text{X}$ products (where X is Cl [panel (a)], Br [panel (b)] and I [panel (c)]).

[0049] Fig. 25 shows XRD patterns of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{X}$ (X = Cl, Br, I) using Li_3PS_4 from THF solvent.

[0050] Fig. 26 shows Arrhenius plots of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{Cl}$ using different Li_3PS_4 precursors (from THF solvent or ACN).

[0051] Fig. 27 shows a SEM image of $\text{Li}_6\text{PS}_5\text{Cl}$.

[0052] Fig. 28 shows the XRD patterns [panel (a)] and the Raman spectra [panel (b)] for lithium argyrodites with different Cl contents.

[0053] Fig. 29 shows the XRD patterns [panel (a)] and analysis of the $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ sample after annealing heat treatment under different temperatures [panel (b)].

[0054] Fig. 30 shows SEM images of the lithium argyrodites with different Cl contents produced in accordance with inventive methods disclosed herein, wherein [panel (a)] is the

SEM image for $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$, [panel (b)] is the SEM image for $\text{Li}_6\text{PS}_5\text{Cl} \cdot 2\text{LiCl}$, and [panel (c)] is the EDX mapping of $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$.

[0055] Fig. 31 shows Arrhenius plots of solvent-synthesized lithium argyrodites (Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ with $x = 0, 0.5, 1, 1.5$ and 2) [panel (a)] and also shows composition dependence of room temperature conductivities and activation energies for lithium argyrodites with excess Cl content [panel (b)].

[0056] Fig. 32 shows cyclic voltammetry curves under scanning rate of 50 mV/s in the range of -0.5 - 5.0 V (vs Li/Li^+) [panel (a)], and the cycling performance of symmetric cells (current density of 0.02 mA cm^{-2}) [panel (b)] for the $\text{Li}_m\text{PS}_n\text{Cl}_o$ samples with different Cl content ($0 \leq o \leq 3$).

[0057] Fig. 33 [panel (a)] shows Nyquist plots of lithium argyrodites with different Cl content Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($x=0, 0.5, 1, 1.5, 2$) at room temperature and [panel (b)] compares the Nyquist plots of $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$.

[0058] Fig. 34 shows the cyclic voltammetry curve of $\text{Li}_5\text{PS}_4\text{Cl}_2$ solid electrolyte in large voltage window up to 10 V (vs Li/Li^+).

[0059] Fig. 35 shows the symmetric cells cycling voltage profiles for Li_7PS_6 solid electrolyte under different current densities ($0.02, 0.03$, and 0.05 mA cm^{-1}).

[0060] Fig. 36 shows the symmetric cells cycling voltage profiles for $\text{Li}_6\text{PS}_5\text{Cl}$ solid electrolyte under different current densities ($0.02, 0.03$, and 0.05 mA cm^{-1}).

[0061] Fig. 37 shows the symmetric cells cycling voltage profiles for $\text{Li}_5\text{PS}_4\text{Cl}_2$ solid electrolyte under different current densities ($0.02, 0.03$, and 0.05 mA cm^{-1}).

[0062] Fig. 38 shows the symmetric cells cycling voltage profiles for $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ solid electrolyte under different current densities ($0.02, 0.03$, and 0.05 mA cm^{-1}).

[0063] Fig. 39 shows the comparison of battery cycling performance of Li/LTO cells with $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ and $\text{Li}_6\text{PS}_5\text{Cl}$ as the solid electrolyte composition under 0.2 C .

MULTIPLE EMBODIMENTS AND ALTERNATIVES

[0064] Methods for wet chemical synthesis of lithium argyrodites, according to multiple embodiments and alternatives, opens new possibilities for synthesizing highly pure and homogenous materials through a simple and scalable manufacturing process. Compared to conventional synthesis methods, methods presented herein according to multiple embodiments and alternatives are scalable, more efficient, easier to prepare, have a shorter synthesis time, and utilize an environmentally friendly and affordable solvent (e.g, ethanol). Moreover, the synthesized product according to multiple embodiments and alternatives exhibits high phase purity, excellent room temperature ionic conductivity, and high stability. Accordingly, inventive methods for wet chemical synthesis of lithium argyrodite as described herein may allow for the success of ASSBs at scales that are practical for serving the mobile electric vehicle market.

[0065] According to multiple embodiments and alternatives, a method for wet chemical synthesis of lithium argyrodites involves dissolving a stoichiometric mixture of precursors (Li_2S , $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ and LiX [where $\text{X} = \text{Cl}, \text{Br}, \text{I}$] as non-limiting examples) in a small quantity of ethanol in an argon atmosphere. Next, drying the mixture above room temperature (i.e. greater than 22°C) under vacuum, or in an inert gas atmosphere, to evaporate the ethanol (no longer than 1 hour, preferably 40-50 minutes), then annealing above 150°C for one hour obtains a final lithium argyrodite product. Further embodiments comprise synthesizing the precursors by dissolving Li_2S and P_2S_5 in ACN, stirring the mixture for eight hours at room temperature, and then filtering the product. The obtained white powder is then dried at 80°C under vacuum ($\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$) followed by a heat treatment above 150°C ($\beta\text{-Li}_3\text{PS}_4$). Further embodiments comprise the use of halide doping by modifying the ratios of LiCl vs. Li_3PS_4 . According to multiple embodiments and alternatives, an argyrodite prepared with an excess amount of 2 moles of chloride achieves a desirable ionic conductivity at room temperature. It

is expected that bromine or iodine doping will have a similar impact on increasing the ionic conductivity of the argyrodite.

[0066] According to multiple embodiments and alternatives, the synthesized argyrodites can be utilized as the electrolyte in an electrochemical energy storage device (such as an ASSB as a non-limiting example). In some embodiments, the electrochemical energy storage device comprises an anode, a cathode, and the synthesized argyrodite as the electrolyte. The anode releases electrons to the circuit and oxides during the electrochemical reaction, the cathode acquires electrons from the external circuit and is reduced during the electrochemical reaction, and the electrolyte is the medium that acts as the ionic conductor. ASSBs utilizing solid electrolyte compositions, prepared according to multiple embodiments and alternatives, achieve a desirable specific capacity likely due to the formation of a more stable solid electrolyte interphase layer and by blocking side reactions.

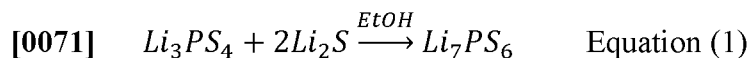
[0067] All examples provided herein are meant as illustrative of various aspects of multiple embodiments and alternatives of wet chemical synthesis of lithium argyrodites. These examples are non-limiting and merely characteristic of multiple alternative embodiments as described and claimed or to-be-claimed herein.

[0068] Example 1 – Wet Chemical Synthesis of Li_7PS_6

[0069] *Synthesis of Li_3PS_4 precursor* – As illustrated in Fig. 7, the Li_2S and P_2S_5 with a stoichiometry of 3:1 is dissolved in acetonitrile (ACN), stirred for 8h at room temperature and then filtrated. The obtained white powder is then dried at 80°C under vacuum to remove excess solvent yielding $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$. Further heat treatment above 150°C produces $\beta\text{-Li}_3\text{PS}_4$.

[0070] *Synthesis of Li_7PS_6 electrolyte* – As illustrated in Fig. 1, a stoichiometric mixture (2:1 molar) of Li_2S and $\beta\text{-Li}_3\text{PS}_4$ is dissolved in a small quantity of anhydrous ethanol (25 ml) in argon atmosphere. Next, the mixture is dried above room temperature (i.e. greater than 22°C) under vacuum or an inert gas atmosphere to evaporate the solvent yielding a white precipitate

(not longer than 1 hour, preferably 40-50 minutes), and then treated above 150°C for 1 hour to obtain a final product (Li₇PS₆). As previously noted, the chemical reaction of β-Li₃PS₄ and Li₂S to produce cubic Li₇PS₆ is:



[0072] *Structural and Morphological Investigation* – The phase composition and crystal structure of the Li₇PS₆ electrolyte synthesized within the scope of embodiments were analyzed using X-ray diffraction (XRD) (Bruker D8 Discover) with nickel-filtered Cu-Kα radiation (λ = 1.5418 Å). The Scherrer equation was used to estimate the crystallite size of the obtained materials. The Scherrer equation, when utilized in XRD, is a formula that relates the size of crystallites in a solid to the broadening of a peak in a diffraction pattern. The Scherrer equation is a simple and well-known expression for obtaining a measure of the crystallite size from XRD peaks. The Scherrer equation is represented by the following formula:

[0073]
$$\tau = (K \lambda) / (\beta \cos \theta) \quad \text{Equation (4)}$$

[0074] where τ is the mean size of the ordered (crystalline) domains, K is a dimensionless shape factor, λ is the X-ray wavelength, β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians, and θ is the Bragg angle.

[0075] The chemical and structural data was obtained from the Raman spectroscopy, which was measured using Renishaw in Via Raman/PL Microscope and a 632.8 nm emission line of a HeNe laser. Raman spectroscopy is a technique used to observe vibration, rotational, and other low-frequency modes in a system. Typically, a sample is illuminated with a laser beam, then electromagnetic radiation from the illuminated spot is collected with a lens and sent through a monochromator. Elastic scattered radiation at the wavelength corresponding to the laser line is filtered out by either a notch filter, edge pass filter, or a band pass filter, while the rest of the collected light is dispersed onto a detector.

[0076] General morphologies of all samples were also investigated using a TESCAN Vega3 scanning electron microscope (SEM).

[0077] *Conductivity and Electrochemical Stability* - Electrochemical impedance spectroscopy (EIS) was carried out to measure the ionic conductivities of samples, synthesized within the scope of embodiments, in the frequency range from 1 MHz to 100 mHz with an amplitude of 100 mV using Bio-Logic VSP300. For the measurements, dense pellets (1/2" diameter) were prepared by cold pressing the powder with C/Al as blocking electrodes at each side and placed in Swagelok cells. A Swagelok cell is typically a cylindrical battery cell that is widely known to one of ordinary skill in the art.

[0078] As expected for pure ionic conductors, EIS spectra present a semi-arc at high frequencies and a straight line at lower frequencies. The intercept of a straight line at the axis is employed to determine the total ionic conductivity of the material. In addition, the temperature dependent spectra were recorded from room temperature (i.e. about 22°C) to 90°C to obtain the Arrhenius plot. An Arrhenius plot displays the logarithm of a reaction rate constant plotted against inverse temperature.

[0079] Swagelok cells were also used to complete cyclic voltammetry (CV) and cycling performance measurements. A CV test is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of the predicted amount. For the CV test, Li/SE/Pt cells were scanned at 50 mV s⁻¹ rate between 0.5 and 5V vs. Li/Li⁺ at room temperature using Bio-Logic VSP 300 potentiostat. For symmetric cell cycling, the Li/SE/Li symmetric cell were assembled and cycled on a battery system (Bio-Logic VSP) with current densities of 50 $\mu\text{A cm}^{-2}$.

[0080] *Results and Discussion*

[0081] Structural Analysis

[0082] In this Example, Li_7PS_6 solid electrolyte was synthesized by reacting Li_3PS_4 and Li_2S in an anhydrous ethanol, and subsequent heat treatment at low temperature (as shown in Fig. 1), according to multiple embodiments and alternatives. Li_3PS_4 has a similar solubility as Li_2S in ethanol and thus made the Li_7PS_6 reaction possible.

[0083] As shown in Fig. 7, the pure phase of Li_7PS_6 product was also obtained by using $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ complex as the precursor to react with Li_2S in ethanol. Fig. 8 illustrates the XRD patterns of Li_7PS_6 solid electrolyte using different precursors: $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ complex and Li_3PS_4 . Fig. 8 shows that the source of Li_3PS_4 has no difference on the Li_7PS_6 phase purity and expands to Li_3PS_4 synthesized from other solid-state methods.

[0084] As shown in Fig. 2 (panel a), the as-synthesized Li_7PS_6 powder was characterized by XRD. Interestingly, the Li_7PS_6 powder synthesized according to multiple embodiments and alternatives displays several sharp peaks at $2\theta=25.5, 30, 31.2^\circ$, corresponding to (220), (311) and (222) planes in cubic HT-phase of Li_7PS_6 (space group $F-43m$). These characteristic diffraction peaks shown in Fig. 2 align with the pure phase of cubic Li_7PS_6 that has been reported previously. The cubic structure of the synthesized product has a unit cell parameter equal to $9.88 \text{ \AA}$ and the crystal size is estimated at 34 nm . As shown in Fig. 2 (panel a), Li_7PS_6 shows totally different diffraction patterns than orthorhombic $\beta\text{-Li}_3\text{PS}_4$ (space group Pnma , $a = 12.997 \text{ \AA}$, $b = 8.081 \text{ \AA}$, $c = 6.143 \text{ \AA}$). Furthermore, due to stoichiometric amounts of reactants and a homogeneity of the liquid preparation method, the final material is free from Li_2S impurity and other crystal phases.

[0085] The Raman spectra of cubic Li_7PS_6 and $\beta\text{-Li}_3\text{PS}_4$ are shown in Fig. 2 (panel b). The precursor Li_3PS_4 exhibits a peak at 421.1 cm^{-1} and this can be attributed to symmetric stretching vibration of $(\text{PS}_4)^{3-}$ (*ortho*-thiophosphate) group in orthorhombic $\beta\text{-Li}_3\text{PS}_4$ structure. Furthermore, a few minor lines at $387.6, 530.2$ and 568.5 cm^{-1} are observed, where the first mode corresponds to a trace of $\text{Li}_4\text{P}_2\text{S}_6$ and its $(\text{P}_2\text{S}_6)^{4-}$ (P–P bond) vibrational mode, and the

latter two refer to the additional $(\text{PS}_4)^{3-}$ vibrational modes. After the reaction, Li_7PS_6 shows a PS_4^{3-} vibrational mode at 421.6 cm^{-1} as expected. A small peak at 497.2 cm^{-1} and broad line around 575 cm^{-1} are probably attributable to, similarly to Li_3PS_4 structure, the additional $(\text{PS}_4)^{3-}$ vibrational modes. Due to a strong ionic character of bonds between S^{2-} and Li^+ ions in the crystal Raman, the lines from $\text{Li}^+-\text{S}^{2-}$ interaction are expected to be weak.

[0086] The XRD pattern of intermediate product after the evaporation of EtOH (as illustrated in Fig. 9), shows that pure phase of Li_7PS_6 exists before heat treatment at $200\text{ }^\circ\text{C}$, suggesting that this reaction happens at room temperature without heating. This also indicates that Li_7PS_6 is unlikely to form an adduct with ethanol, which makes it easy to remove the solvent.

[0087] To further understand the reaction mechanism, the dissolution and re-precipitation process of Li_3PS_4 in ethanol was studied and compared with the case in acetonitrile. Fig. 10 demonstrates that Li_3PS_4 forms a complex of $\text{Li}_3\text{PS}_4\cdot(\text{ACN})_2$ in acetonitrile reverting to pure phase back after heat treatment. In contrast, the re-precipitated Li_3PS_4 material from ethanol shows unknown crystal structure after drying at $80\text{ }^\circ\text{C}$ and exhibits amorphization after heating at above 150°C (see Fig. 11). The reference bands in Fig. 11 show the Li_3PS_4 re-prec is different with Li_3PS_4 and $\text{Li}_3\text{PS}_4\text{ACN}$. As shown in Fig. 12, the structural change of Li_3PS_4 in ethanol is further supported by the Raman spectra, in which the characteristic peak of $(\text{PS}_4)^{3-}$ group vibration is not observed. Nevertheless, with the existence of Li_2S in ethanol, the cubic phase of Li_7PS_6 can be successfully produced from Li_3PS_4 without any other crystal phase.

[0088] Morphological Analysis

[0089] According to multiple embodiments and alternatives, the morphology variation from Li_3PS_4 precursor to Li_7PS_6 product was also analyzed using SEM. As shown in Fig. 3 (panel b), the Li_3PS_4 sample prepared from ACN has an interesting flake-like morphology. In contrast, as shown in Fig. 3 (panel a), the Li_7PS_6 product shows a granular nano-sized

morphology (agglomerated particles of about 100 nm size). The difference in morphology of these samples is related to the solvent involved in the synthesis. As shown in Fig. 13, Li_3PS_4 dissolved in ethanol and the re-precipitated sample displays a grainy shape.

[0090] EDX analysis of the Li_3PS_4 precursor and final Li_7PS_6 product is shown in Fig. 4. The distribution of P and S atoms is practically the same for both materials, indicating homogeneity through liquid synthesis methods. The calculated ratio between P and S atoms in these samples are 1:3.2 and 1:4.6, respectively, which can indicate elemental disturbance at the surface of the materials.

[0091] Conductivity and Stability Measurements

[0092] EIS were employed to measure the conductive properties of both cubic Li_7PS_6 and $\beta\text{-Li}_3\text{PS}_4$. As shown in Fig. 5 (panel a), the synthesized Li_7PS_6 has an ionic conductivity of about 0.11 mS cm^{-1} to 0.5 mS cm^{-1} at about room temperature, which is a much higher value compare to a previous report from the liquid synthesis of Li-P-S argyrodite. Furthermore, the synthesized Li_7PS_6 has an ionic conductivity of about 1.5 mS cm^{-1} at about 90°C . The Nyquist plots of Li_7PS_6 and $\beta\text{-Li}_3\text{PS}_4$ (as shown in Fig. 14) show both solid electrolytes have decreased total resistance with increasing temperature. Compared with $\beta\text{-Li}_3\text{PS}_4$, Li_7PS_6 exhibits faster Li-ion mobility at elevated temperatures. For instance, the ionic conductivity of Li_7PS_6 is $1.5 \times 10^{-3} \text{ S cm}^{-1}$ at 90°C while $1.0 \times 10^{-3} \text{ S cm}^{-1}$ for Li_3PS_4 at the same temperature. The activation energy of Li_7PS_6 is determined to be $38.73 \text{ kJ mol}^{-1}$ (0.4 eV), whereas Li_3PS_4 is equal to $32.39 \text{ kJ mol}^{-1}$ (0.336 eV).

[0093] Fig. 5 (panel b) compares the conductivities and productivity for Li_7PS_6 prepared through different methods: $3 \times 10^{-5} \text{ S cm}^{-1}$ (conventional solid state reaction at 650°C for 7 days, represented by “Ref 32” in Fig. 5), $8 \times 10^{-5} \text{ S cm}^{-1}$ (conventional crystal powder from solid state reaction, 40 hours, represented by “Ref 12, 13” in Fig. 5), and methods according to the present disclosure: $1.1 \times 10^{-4} \text{ S cm}^{-1}$ (liquid synthesis approach, 2 hours, represented by “This work” in

Fig. 5). In Fig. 5 (panel b), the lighter bars represent the productivity and the darker bars represent the conductivities. Both synthetic approaches of solid-state reaction and mechanical milling require the reaction time longer than 40 hours and the yielded products show conductivity values of 10^{-5} - 10^{-4} S cm⁻¹. In contrast, the Li₇PS₆ synthesis according to multiple embodiments and alternatives can be completed in 2 hours. The findings from the present disclosure suggest that reacting and nucleating Li₇PS₆ crystals straight from the solution is beneficial for the final ionic conductivity. In addition, the ionic conductivity value of Li₇PS₆ from the present disclosure is also close to other Li₂S-P₂S₅ family materials previously prepared by solid-state methods (e.g., glasses and glass-ceramics).

[0094] As shown in Fig. 6 (panel a), the electrochemical stability between the synthesized Li₇PS₆ and metallic Li was investigated by cyclic voltammogram (CV) of a Li/ Li₇PS₆/Pt cell, in which Li and Pt serve as the reference/courter electrode and working electrodes, respectively. The potential was scanned from -0.5 to 5.0V (vs. Li⁺/Li) at a scan rate of 50 mVs⁻¹. As illustrated in Fig. 6 (panel a), for both solid electrolytes (cubic Li₇PS₆ and β-Li₃PS₄), a pair of reversible oxidation and reduction peaks is observed at around 0 V (vs. Li⁺/Li) without any other side reaction. Furthermore, the cathode current below 0 V is a Li deposition on working electrode (Li⁺ + e⁻ → Li), whereas the anode current above 0 V results from reversible lithium dissolution. The CV curves illustrated in Fig. 6 (panel a) indicate that Li₇PS₆, synthesized in accordance with multiple embodiments and alternatives, exhibits as good stability with Li anode as Li₃PS₄ over a broad electrochemical window (up to 5 V).

[0095] A symmetric cell of Li/Li₇PS₆/Li was configured to demonstrate the compatibility of Li₇PS₆ solid electrolyte with metallic Li under a current density of 50 μAcm⁻² at room temperature and the results are shown in Fig. 6 (panel b). The values of overpotential for the symmetric cell are lower than 20 mV with a slight increase as cycling continues, suggesting the possible interfacial reactions between Li anode and Li₇PS₆ solid electrolyte. Nevertheless,

after cycling, shiny Li surface was still observed when peeling it off from Li_7PS_6 solid electrolyte in the symmetric cell. The XRD patterns of the solid electrolyte pellet after cycling (shown in Fig. 15) show characteristic peaks of Li_7PS_6 , which indicates that the interfacial reaction is not severe.

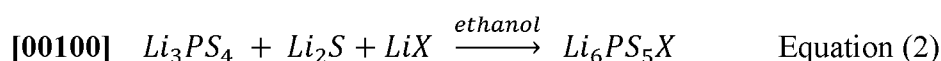
[0096] In summary, crystalline lithium argyrodite solid electrolyte was rapidly and economically synthesized through the stoichiometric chemical reaction of Li_2S and Li_3PS_4 in ethanol medium. The synthesized Li_7PS_6 has the room temperature ionic conductivity of at least 0.11 mS cm^{-1} at room temperature and 1.5 mS cm^{-1} at 90°C , a desirable value among pure materials prepared through liquid synthesis, and 40% higher than those crystalline Li_7PS_6 powders from other synthesis methods (i.e. solid-state reaction and ball milling). Furthermore, the synthesized Li_7PS_6 is highly compatible with the metallic Li anode. Accordingly, methods for wet chemical synthesis of lithium argyrodites, according to multiple embodiments and alternatives, leads to high purity phase of Li_7PS_6 material with scalable and simple processing steps. Moreover, inventive methods for wet chemical synthesis of lithium argyrodites further position Li_7PS_6 as a desirable electrolyte candidate in the large-scale all-solid-state battery technology.

[0097] **Example 2 – Wet Chemical Synthesis of $\text{Li}_6\text{PS}_5\text{X}$, where X = Cl, Br, or I**

[0098] Synthesis of Li_3PS_4 precursor – As illustrated in Fig. 7, the Li_2S and P_2S_5 with a stoichiometry of 3:1 is dissolved in acetonitrile (ACN), stirred for 8h at room temperature and then filtrated. The obtained white powder is then dried at 80°C under vacuum to remove excess solvent yielding $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$. Further heat treatment above 150°C produces $\beta\text{-Li}_3\text{PS}_4$.

[0099] *Synthesis of $\text{Li}_7\text{PS}_5\text{X}$ electrolyte* – As illustrated in Fig. 16, the $\text{Li}_6\text{PS}_5\text{X}$ electrolyte (where X = Cl, Br, or I) was efficiently synthesized using a wet chemical method according to multiple embodiments and alternatives. A stoichiometric mixture of Li_2S , $\text{Li}_3\text{PS}_4 \cdot (\text{ACN})_2$ and LiX (X = Cl, Br, I) was dissolved in a small quantity of anhydrous ethanol (25 ml) in argon

atmosphere. To bypass the P_2S_5 insolubility problem, pure Li_3PS_4 precursor was used. Next, the solvent was evaporated at 90°C under vacuum until a white precipitate was present (not longer than 1 hour, preferably 40-50 minutes). The heat treatment continued above 150°C (1 hour) and got a final product (Li_6PS_5Cl , Li_6PS_5Br , and Li_6PS_5I respectively) synthesized according to multiple embodiments and alternatives. As previously noted, the chemical reaction for the synthesis of Li_6PS_5X electrolyte is expressed by:



[00101] *Structural and Morphological Investigation* – The phase composition and crystal structure of the final product were examined using X-ray diffraction (Bruker D8 Discover) with nickel-filtered Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The crystallite size of the obtained materials was estimated using the Scherrer equation. In addition, the chemical and structural data was obtained from the Raman spectroscopy measured by Renishaw in Via Raman/PL Microscope with a 632.8 nm emission line of a HeNe laser. TESCAN Vega3 scanning electron microscope (SEM) was used to study the morphology of the samples synthesized according to multiple embodiments and alternatives.

[00102] *Electrochemistry and conductivity* - Electrochemical impedance spectroscopy (EIS) were performed to measure the ionic conductivities of produced samples in the frequency range from 1 MHz to 100 mHz with an amplitude of 50 mV using Bio-Logic VSP300. Measurements were done using dense pellets (1/2" diameter) prepared by a cold pressing of powders between two electrodes of conductive carbon on aluminum current collector (blocking electrode) and placing them in homemade press cells. As expected for pure ionic conductor, EIS spectra present a semi-arc at high frequencies and a straight line at lower frequencies. The straight line intercept at the X axis is employed to determine the total ionic conductivity of the material. In addition, the temperature dependent spectra were recorded from room temperature to 90°C to obtain the Arrhenius plot. Swagelok cells were also used to complete cyclic voltammetry (CV)

and cycling performance measurements. For CV test, Li/SE/Pt cells were scanned at 50 mV s^{-1} rate between -0.5 and 5 V vs. Li/Li^+ at room temperature using. For symmetric cell cycling, the Li/SE/Li symmetric cell were assembled and cycled on a battery system (Bio-Logic VSP) with current densities of $50 \mu\text{A cm}^{-2}$.

[00103] *Results and Discussion*

[00104] Crystal Structure Analysis of Anionic Substituted $\text{Li}_6\text{PS}_5\text{X}$

[00105] As illustrated in Fig. 16, for $\text{Li}_6\text{PS}_5\text{X}$ (where $\text{X} = \text{Cl}, \text{Br}$ or I) synthesis, stoichiometric mixtures of Li_3PS_4 , Li_2S and LiX (where $\text{X} = \text{Cl}, \text{Br}$ or I) were dissolved in anhydrous ethanol, stirred, and followed by a heat treatment above 150°C , yielding white powders for halide doped lithium argyrodites. The final products synthesized according to multiple embodiments and alternatives were characterized by XRD (as shown in Fig. 17), and were identified as $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{Br}$, and $\text{Li}_6\text{PS}_5\text{I}$, corresponding to LiCl , LiBr and LiI reactants, respectively. Similar to the case of the pure Li_7PS_6 powder from Example 1, all halide doped samples display several sharp peaks at $2\theta \approx 25.5, 30, 31.2^\circ$, attributing to (220), (311), and (222) planes in cubic phase (space group $F-43m$), but with a slight peak shift due to the subtle change on unit cell parameters. The set of unit cell parameter, crystal size, ionic radius of the halides and sulfide anions for Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{X}$ are presented in Table 1.

[00106] **Table 1. Structural and Spectral Properties of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{X}$ lithium argyrodite samples.**

Sample	Crystal Size (nm)	Unit cell parameter (Å)	Ionic radius (pm)	Raman shift (cm^{-1})	FWHM (cm^{-1})	E_a (kJ/mol)	E_a (eV)
Li_7PS_6	34	9.88	(S^{2-}) 170	421.5	10.7	41.46	0.430

Li ₆ PS ₅ Cl	45	9.84	(Cl ⁻) 167	425.1 392.6	10.7 16	38.57	0.400
Li ₆ PS ₅ Br	39	9.89	(Br ⁻) 182	423.3 388.8	9 12	40.24	0.417
Li ₆ PS ₅ I	32	9.95	(I ⁻) 206	422.7 390.1	11.6 17	40.47	0.419

[00107] Based on the results shown in Table 1, the lattice parameter a decreases from 9.88 Å for Li₇PS₆ to 9.84 Å for Li₆PS₅Cl and then increases to 9.89 Å for Li₆PS₅Br and 9.95 Å for Li₆PS₅I, respectively. This trend is consistent with the ion's radius variations, due to Cl⁻ (167 pm) < S²⁻ (170 pm) < Br⁻ (182 pm) < I⁻ (206 pm). Larger anions (Br⁻ and I⁻) lead to the expansion of the lattice parameter in the cubic structure.. This observation fits well with the trend from the previous experimental reports on the Li₆PS₅X series. Due to stoichiometric amounts of used ingredients in liquid-based synthesis method, the final products are mostly free from impurities. Only in the case of Li₆PS₅Br, were trace amounts of LiBr observed. It is important to mention that the preparation time of these solid electrolyte materials according to the disclosure herein is only about 2 hours. On the other hand, the preparation time for ball-milling takes at least 5 hours (and up to 4 days), not even counting the much longer heating/cooling process required for full crystallization to occur (e.g. 5 hours and up to 7 days).

[00108] To confirm the crystal structure, the Raman spectra of Li₆PS₅X samples (Li₆PS₅Cl, Li₆PS₅Br, and Li₆PS₅I), were collected and compared with that of pure Li₇PS₆, as shown in Figure 18. Similar with Li₇PS₆ material, all three halide doped samples (Li₆PS₅X) exhibit strong lines in the range between 422 and 425 cm⁻¹ attributed to PS₄⁻³ ion vibration and the minor lines at about 390 cm⁻¹. The exact line positions and their full width at half maximum (FWHM) values are shown in Table 1 (above). The results indicate that PS₄⁻³ ion vibration is

influenced by the surrounding halide ions which likely change the force constants and cause the evident peak shift. The Raman shift of PS_4^{-3} ion vibration decreases while the unit cell of argyrodite increases. The minor line mode can correspond to a trace of $\text{Li}_4\text{P}_2\text{S}_6$ and its $\text{P}_2\text{S}_6^{-4}$ vibrational mode. For comparison, the Li_7PS_6 has a similar PS_4^{-3} vibrational mode at 421.6 cm^{-1} as expected.

[00109] The morphology of the products synthesized according to present embodiments were also analyzed by SEM images. As previously stated, the solvent may play a role in the final morphology of the material. As shown in Fig. 19, the morphology of the $\text{Li}_6\text{PS}_5\text{X}$ material series was compared to the Li_7PS_6 product prepared from ethanol. Fig. 19 illustrates that the reaction of Li_3PS_4 , Li_2S , and LiX in ethanol solvent results in grainy nanosized morphology (agglomerated particles of about 500 nm size) as expected.

[00110] In addition, the EDX maps of the $\text{Li}_6\text{PS}_5\text{X}$ (see Fig. 23) show uniform distribution of P, S, and X (Cl, Br, and I) atoms, suggesting a homogeneity in the final product after the liquid synthesis method, according to multiple embodiments and alternatives.

[00111] Electrochemical performance of Li_7PS_6 electrolyte from liquid phase

[00112] The conductivity measurements in a blocking cell show that $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$ materials prepared according to the synthesis method disclosed herein have higher ionic conductivities than pure Li_7PS_6 samples. In particular, their values at room temperatures are $1.4 \times 10^{-4}\text{ S cm}^{-1}$ and $1.2 \times 10^{-4}\text{ S cm}^{-1}$ compared to $1.1 \times 10^{-4}\text{ S cm}^{-1}$ of Li_7PS_6 material. This enhancement on ionic conductivity is closely related with the replacement of Cl and Br to S ions, which results in more defects in $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$. As expected, the $\text{Li}_6\text{PS}_5\text{I}$ shows the lower ionic conductivity of $2.9 \times 10^{-5}\text{ S cm}^{-1}$ compared with its Cl- and Br- analogues. This effect was recently explained and experimentally proven by correlating the lattice softness with the ionic transport. The latest results suggest that the softer bonds lower the activation energy and simultaneously decrease the moving ion prefactor. The addition of Cl, Br, or I ions to the

crystal structure leads to an obvious change in the unit cell volume (as illustrated in the XRD patterns shown in Fig. 17), as well as the lattice site disorder. The decreasing disorder increases the activation barrier of the ionic transport. The electrochemical performance results further confirm these theoretical findings.

[00113] In addition to room temperature conductivity, the total activation energy of the prepared samples was calculated from the temperature dependent EIS spectra. Fig. 20 shows Arrhenius plots which reflect the temperature dependence of ionic conductivities for $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) samples and pristine Li_7PS_6 . All materials show linear relations of ionic conductivity vs temperature, and the slopes are proportional to the activation energy (E_a) for Li-ion conduction according to the following equation:

[00114] $\sigma = \sigma_0 e^{\frac{E_a}{kT}}$ Equation (5)

[00115] where σ is the photo-ionization cross-section, σ_0 is the pre-exponential photo-ionization cross-section, E_a is the activation energy, k is Boltzmann's constant, and T is the temperature. The activation energies of $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{Br}$, and $\text{Li}_6\text{PS}_5\text{I}$ are estimated to be $38.57 \text{ kJ mol}^{-1}$ (0.399 eV), $40.24 \text{ kJ mol}^{-1}$ (0.417 eV), and $40.47 \text{ kJ mol}^{-1}$ (0.419 eV) while Li_7PS_6 is equal to $41.46 \text{ kJ mol}^{-1}$ (0.430 eV), as specified in Table 1. The comparison indicates that introducing halide ions ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) reduces the barrier for Li ion mobile along the framework and thus decreases the values of activation energy. The total activation energies of halide doped materials show lower values than pure Li_7PS_6 . The $\text{Li}_6\text{PS}_5\text{Cl}$ sample has the lowest activation energy and also shows the best conductivity among all doped samples. This suggests that $\text{Li}_6\text{PS}_5\text{Cl}$ has the lowest barrier for lithium ions to move along the material. The main reason for the best conductivity of $\text{Li}_6\text{PS}_5\text{Cl}$ is due to the distribution of disorder of Cl ions over the 4a and 4c sites together, which provides both high Li^+ intercage jump rates and doublet jump rates in the $\text{Li}_6\text{PS}_5\text{Cl}$ structure.

[00116] For a solvent-based synthesis method, Li_3PS_4 is the most important precursor to produce high purity $\text{Li}_6\text{PS}_5\text{X}$ argyrodites. Previously, Li_3PS_4 was reported to yield either flaky or chunky morphology from different solvent-based processes. Accordingly, Li_3PS_4 precursors from two synthesis solvents (ACN and THF) were used to prepare $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$) argyrodites following the inventive methods disclosed herein. The synthesized $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$) solid electrolytes were characterized by XRD for phase identification (Fig. 25), which confirm the products of $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$ (containing a small amount LiBr). Fig. 26 shows the Arrhenius plots of $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$, which display similar ionic conductivities (at least 0.1 mS cm^{-1}) between $\text{Li}_6\text{PS}_5\text{Cl}$ (or $\text{Li}_6\text{PS}_5\text{Br}$) samples prepared using Li_3PS_4 from either ACN or THF. As shown in Fig. 26, $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Br}$ displayed an ionic conductivity of about 0.11 mS cm^{-1} to 0.5 mS cm^{-1} at room temperature, and an ionic conductivity of about 1.5 mS cm^{-1} at about 90°C . SEM image shows granular morphology (Fig. 27). These observations indicate that the source of Li_3PS_4 doesn't have a significant influence on the structure, conductivity or morphology of solvent-synthesized $\text{Li}_6\text{PS}_5\text{X}$ materials.

[00117] CV Testing in a Symmetric Lithium Cell

[00118] CV was employed to evaluate the electrochemical stability of solvent-synthesized $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{I}$) materials against Li metal in a voltage window of 0.5-5.0 *vs* Li/Li^+ (Fig. 21). The assembled cells have structure of $\text{Li}/\text{Li}_6\text{PS}_5\text{X}/\text{SS}$, with Li as the reference/courter electrode and stainless steel (SS) as the working electrode. For all $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{I}$) materials, only one pair of oxidation and reduction peaks are observed near 0 V *vs* Li/Li^+ , attributing to the lithium dissolution ($\text{Li} \rightarrow \text{Li}^+ + e^-$) and lithium deposition ($\text{Li}^+ + e^- \rightarrow \text{Li}$), respectively. There is no other peak observed up to 5 V, suggesting good electrochemical stability of $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{I}$) solid electrolyte against Li metal in a cell structure of $\text{Li}/\text{SE}/\text{SS}$. Among them, $\text{Li}_6\text{PS}_5\text{Cl}$ shows a highly desirable oxidative/reductive current.

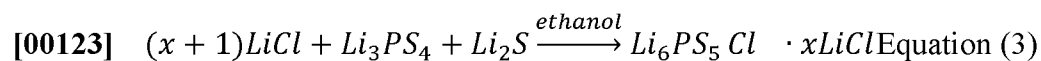
[00119] Symmetric cells of Li/Li₆PS₅X/Li were assembled to evaluate the long-term compatibility of liquid synthesized Li₆PS₅X with Li metal at room temperature. All the cells were cycled at room temperature with a current density of 20 $\mu\text{A cm}^{-2}$. Fig. 21 (panel b) and Figure 22 show smooth cycling profiles for for these symmetric cells with Li₆PS₅X (X = Br, Cl, I) as solid electrolytes and the resulting voltages are stable over 3000 mins (50 cycles). However, the voltage for Li₆PS₅X-based symmetric cells follows a trend of (Li₆PS₅I)>(Li₆PS₅Br)>(Li₆PS₅Cl), which is in reverse with the ionic conductivity of solid electrolyte. Li₆PS₅Cl has a desirable ionic conductivity and lowest resistance, thus the lowest voltage under the same current density.

[00120] In conclusion, Li₆PS₅X argyrodite materials were successfully synthesized utilizing the synthesis method according to multiple embodiments and alternatives. The conductivity values at room temperature of the synthesized materials reached as high as $1.4 \times 10^{-4} \text{ S cm}^{-1}$. Accordingly, inventive methods for wet chemical synthesis of lithium argyrodites, according to multiple embodiments and alternatives, also produce materials with high ionic conductivity, the possibility of further halide substituting tuning, and easier fabrication prospects. A significant advantage of the wet chemical synthesis method within the scope of embodiments is scalability, production of high quality thin film electrolytes, and selenium impregnation of electrodes. In addition, the shorter and more convenient material processing steps, without the ionic conductivity decrease, is an important advantage of the current method for wet chemical synthesis of lithium argyrodites.

[00121] **Example 3 – Excess Chloride Doping Effect on Lithium Argyrodite Solid Electrolyte**

[00122] *Materials Synthesis* – Since Li₆PS₅Cl exhibited a desirable ionic conductivity amongst three halogen ions, it was selected to study the effect of excess Cl content on the crystal structure, ionic conductivity, and electrochemical stability of LiCl rich argyrodites

$\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$). Accordingly, said $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$) materials were synthesized by dissolving Li_2S , LiCl and $\beta\text{-Li}_3\text{PS}_4$ in ethanol in an argon atmosphere, according to multiple embodiments and alternatives. In particular, Li_2S and LiCl were first dissolved in ethanol, followed by the addition of Li_3PS_4 . The mixture was stirred for 0.5 hours and then dried above room temperature (i.e. 90°) under vacuum to evaporate the ethanol and then annealed above 150°C to collect white powder. The Cl content in $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$) was tuned by controlling the amount of LiCl precursor. According to multiple embodiments and alternatives, the following ratios of $\text{LiCl}:\text{Li}_3\text{PS}_4$ were controlled at 1:1, 1.5:1, 2:1, 2.5:1, and 3:1 to obtain the samples of $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{Cl} \cdot 0.5\text{LiCl}$ (or $\text{Li}_{6.5}\text{PS}_5\text{Cl}_{1.5}$), $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ (or $\text{Li}_7\text{PS}_5\text{Cl}_2$), $\text{Li}_6\text{PS}_5\text{Cl} \cdot 1.5\text{LiCl}$ (or $\text{Li}_{7.5}\text{PS}_5\text{Cl}_{2.5}$), and $\text{Li}_6\text{PS}_5\text{Cl} \cdot 2\text{LiCl}$ (or $\text{Li}_8\text{PS}_5\text{Cl}_3$), respectively. The chemical reaction is represented by:



[00124] *Materials Characterization* – To perform ionic conductivity measurements, 100 mg of the synthesized materials were pressed between carbon-coated aluminum (serving as blocking electrodes) into pellets under high pressure (i.e. 300 MPa) to a disk roughly 10 mm in diameter and 50 mm thick. The pellets were tested via a pressed cell using electrochemical impedance spectroscopy (EIS) and Arrhenius activation energy measurements in the frequency range of 5MHz-1Hz with an amplitude of 100 mV using Bio-Logic VSP300.

[00125] *Results and Discussion*

[00126] Cl-Doping Content Affects the Phase Purity

[00127] A method for wet chemical synthesis of lithium argyrodites was employed to synthesize Li_7PS_6 with different amount of Cl doping, with a general formula of $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$). As previously noted, the Cl content was controlled by tuning the stoichiometric ratio of LiCl precursor vs Li_3PS_4 (from 1:1 to 3:1) to obtain a series of samples ($\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_6\text{PS}_5\text{Cl} \cdot 0.5\text{LiCl}$, $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$, $\text{Li}_6\text{PS}_5\text{Cl} \cdot 1.5\text{LiCl}$, and $\text{Li}_6\text{PS}_5\text{Cl} \cdot 2\text{LiCl}$).

[00128] Fig. 28 (panel a) shows both the XRD patterns of $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ materials containing different amounts of Cl content as well as pure Li_7PS_6 without any Cl doping. Without Cl doping, cubic phase of pure Li_7PS_6 (space group F-43m) was obtained with the characteristic diffraction peaks at $2\theta=25.5, 30, 31.2^\circ$ corresponding to (220), (311) and (222) planes, respectively. When small amounts of LiCl are introduced, $\text{Li}_6\text{PS}_5\text{Cl}$ has almost identical diffraction patterns to those of Li_7PS_6 , suggesting the formation of a solid solution where Cl^- replaces S^{2-} . As Cl content is increased, a secondary phase of LiCl ($2\theta=34.9^\circ, 49.9^\circ$) is observed in addition to the dominant phase of $\text{Li}_6\text{PS}_5\text{Cl}$, and peak intensity continually increases with increasing LiCl. This observation indicates that the excess Cl cannot properly enter the $\text{Li}_6\text{PS}_5\text{Cl}$ structure at highly doped samples after 200 °C heating treatment; instead, heterogeneous composite electrolytes of $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ are formed from the solvent-based synthesis method.

[00129] To study whether Cl can enter the $\text{Li}_6\text{PS}_5\text{Cl}$ structure at a higher temperature, the obtained $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ sample was further annealed in an Argon filled environment under 350 °C and 550 °C for 6 hours, respectively. Although LiCl diffraction peaks are still observed in annealed samples (as shown in Fig. 29), the weight ratio of LiCl to $\text{Li}_6\text{PS}_5\text{Cl}$ decreases as the annealing temperature increases, indicating that excess Cl can partially enter $\text{Li}_6\text{PS}_5\text{Cl}$ structure after high temperature annealing causing an increase of ionic conductivity ($\sim 1.9 \cdot 10^{-3} \text{ mS cm}^{-1}$ for a sample annealed at 550 °C).

[00130] Fig. 28 (panel b) shows the Raman spectra of Li_7PS_6 and Cl-doped samples. The samples synthesized according to multiple embodiments and alternatives all exhibited a strong peak around $421\text{--}425 \text{ cm}^{-1}$, corresponding to the symmetric stretching mode of the P-S bond in the $(\text{PS}_4)^{3-}$ vibrational mode. This peak is also the primary vibrational mode for argyrodite-type materials. The Cl-doping leads to a slight right shift of the dominate peak (to 425 cm^{-1}) and a broad bump around 575 cm^{-1} which is attributed to the asymmetric PS_4^{3-} vibrational

mode. However, the excess amount of LiCl does not result in an obvious change on Raman spectra.

[00131] Fig. 30 shows the SEM images of Li_7PS_6 , $\text{Li}_6\text{PS}_5\text{Cl}$, $\text{Li}_5\text{PS}_4\text{Cl}_2$ samples, produced in accordance with inventive methods disclosed herein. The SEM images (panels (a) and (b)) of the $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ and $\text{Li}_6\text{PS}_5\text{Cl} \cdot 2\text{LiCl}$ materials exhibit similar granular morphologies and homogeneous S, P, and Cl EDX mapping (panel c)).

[00132] Conductivities Depend on Cl-Doping

[00133] The Li-ion conductivities of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($x=0, 0.5, 1, 1.5$, and 2) were evaluated by the electrochemical impedance spectra (EIS) measurements. For EIS tests, all powder samples were cold-pressed under 360 MPa with Al/C foils as the blocking electrodes. Fig. 31 (panel a) shows the Arrhenius plots of Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($x=0, 0.5, 1, 1.5$, and 2) with the temperature range up to 90°C . The conductivities of all samples increase linearly with increasing temperatures, and the slopes reflect the activation energy barriers for Li-ion diffusion across the crystalline framework. The compositional dependence between conductivities and activation energies for $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($0 \leq x \leq 2$) materials is shown in Fig. 31 (panel b). As Cl content increases, the room temperature ionic conductivity increases from 0.34 mS cm^{-1} for $\text{Li}_6\text{PS}_5\text{Cl}$ to the desirable value of 0.53 mS cm^{-1} for $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ and then decreases beyond it. Among them, $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ exhibits the highest ionic conductivity (0.53 mS cm^{-1} at room temperature) and the lowest activation energy (0.29 eV).

[00134] Fig. 33 panel (a) shows the Nyquist plots of lithium argyrodites with different Cl content Li_7PS_6 and $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ ($x=0, 0.5, 1, 1.5, 2$) at room temperature and panel (b) compares the Nyquist plots of $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$. All the spectra consist of a semicircle at high frequency (the total resistance) and a spike at lower frequency (Li-diffusion from blocking electrode). In the case of $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$, excess Cl exists in the form of LiCl instead of entering into the argyrodite's structure, thus the increased ionic conductivity can be

explained by the space-charge effect in composites. Similar with other composites, the slight excess amount of LiCl may cause less resistance for the charged particles, which leads to enhanced Li-ion conductivity for the parent electrolyte ($\text{Li}_6\text{PS}_5\text{Cl}$). However, when the LiCl content is high, it will impede the forward motion of Li-ions since LiCl displays a worse room temperature conductivity ($10^{-7} \text{ S cm}^{-1}$) than $\text{Li}_6\text{PS}_5\text{Cl}$. Notably, $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ also exhibits the lowest activation energy of 0.29 eV, in comparison with 0.39 eV for $\text{Li}_6\text{PS}_5\text{Cl}$.

[00135] $\text{Li}_5\text{PS}_4\text{Cl}_2$ shows better electrochemical performance

[00136] Cyclic voltammetry (CV) was employed to evaluate the electrochemical stabilities of Cl-doped $\text{Li}_m\text{PS}_n\text{Cl}_o$ samples with Li metal anode. The cell structure of $\text{Li}/\text{Li}_{x+5}\text{PS}_{6-x}\text{Cl}_o/\text{SS}$ was constructed in a Swaglock cell, with metallic Li serving as the reference electrode and stainless-steel (SS) acting as the working electrode. The CV scanning was collected in the potential range of -0.5 to 5 V vs. Li/Li^+ at a scan rate of 50 mV s⁻¹.

[00137] As shown in Fig. 32 (panel a), there is only a pair of oxidation (Li dissolution, $\text{Li} \rightarrow \text{Li}^+ + e^-$) and reduction (Li deposition, $\text{Li}^+ + e^- \rightarrow \text{Li}$) peaks near 0 V vs Li/Li^+ without other side reactions, indicating good electrochemical stability with a Li anode. $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ shows the highest values of anodic/cathodic current. In addition, symmetric cells of $\text{Li}/\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}/\text{Li}$ were assembled to study long-term compatibility against Li metal. Figure 32 (panel b) displays smooth voltage profiles for three solid electrolytes (Li_7PS_6 , $\text{Li}_6\text{PS}_5\text{Cl}$ and $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$) under a constant current density of 0.02 mA cm⁻¹, suggesting good cyclability of these solid electrolytes in symmetric cells. Among the three solid electrolytes, $\text{Li}_6\text{PS}_5\text{Cl} \cdot \text{LiCl}$ exhibits the lowest polarization. $\text{Li}_5\text{PS}_4\text{Cl}_2$ also exhibits desirable values of anodic/cathodic current in CV curves, suggesting the lowest resistance in the $\text{Li}/\text{Li}_5\text{PS}_4\text{Cl}_2/\text{SS}$ cell. Fig. 34 shows the CV scan of Li_5PSCl_2 carried out in a wider electrochemical window up to 10 V vs. Li/Li^+ . The CV curves are relatively flat in the range of 0.5-10 V except minor peaks around 7.5 V.

[00138] As illustrated in Figs. 35-38, the Li/Li₅PS₄Cl₂/Li symmetric cell was demonstrated to cycle well under different current densities (0.02, 0.03 and 0.05 mA cm⁻¹). By replacing nonbonded S⁻² with Cl in Li₆PS₅Cl, Li₅PS₄Cl₂ is believed to increase the interface stability. When higher densities are applied (as shown in Fig. 38), Li₆PS₅Cl·LiCl was also demonstrated to show better electrochemical stability with Li anode in comparison with Li₆PS₅Cl, Li₇PS₆, and Li₅PS₄Cl₂ in symmetric cells (Figs. 35-37).

[00139] In summary, a solvent-based synthesis method according to multiple embodiments and alternatives was employed to investigate the effects of halide anion doping on the structure and properties of liquid synthesized lithium argyrodites. Pure phase Li₆PS₅X (X = Cl, Br, I) was obtained through a stoichiometric reaction of LiX, Li₂S and Li₃PS₄ in ethanol solvent. In line with solid-state synthesized Li₆PS₅X materials, Li₆PS₅Cl argyrodite showed a desirable room temperature ionic conductivity of 0.34 mS cm⁻¹, followed by Li₆PS₅Br and then Li₆PS₅I. When excess Cl was introduced, Li₆PS₅Cl·xLiCl composites were obtained instead of a solid solution, suggesting excess Cl cannot enter the argyrodite structure. As Cl content increased, Li₆PS₅Cl·LiCl composite electrolyte exhibited a desirable ionic conductivity of 0.53 mS cm⁻¹ at room temperature (5 × 10⁻³ S cm⁻¹ at 90 °C), which then decreased as Cl content was further increased. The CV and symmetric cell cycling results indicate that solvent-synthesized halide doped lithium argyrodites (Li₆PS₅Cl, Li₆PS₅Br and Li₆PS₅I, Li₆PS₅Cl·LiCl) had good electrochemical stability with Li metal.

[00140] **Example 4 – Electrochemical Energy Storage Device Fabrication**

[00141] *Synthesis* - The battery performance of the solid electrolytes, synthesized according to multiple embodiments and alternatives, was tested with Li₄Ti₅O₁₂ (LTO)/Li cells, wherein LTO serves as the cathode and lithium as the anode in the cell (as non-limiting examples). To prepare the electrode, LTO nanopowder, polyvinylidene fluoride (PVDF) and Super P carbon black (80:10:10 in weight ratio) were mixed in N-methylpyrrolidone (NMP) to form a

homogeneous slurry which was subsequently coated on aluminum foil. The prepared electrodes, with an active material loading of around 2.4 mg cm^{-2} , were dried at 80°C for 24 h under vacuum prior to use. Thin Li foil ($\sim 120 \text{ }\mu\text{m}$, as a non-limiting example) was used as the anode. The solid electrolyte compositions ($\text{Li}_6\text{PS}_5\text{Cl}$ or $\text{Li}_6\text{PS}_5\text{Cl}\cdot\text{LiCl}$ as non-limiting examples) were cold-pressed to dense pellets with a thickness of around $500 \text{ }\mu\text{m}$ and $\frac{1}{2}$ inch diameter. Prior to electrochemical tests, trace amount of propylene carbonate/LiTFSI (Lithium bis(trifluoromethanesulfonyl)imide) electrolyte was added at both sides of the solid electrolyte pellet. Charge and discharge tests were performed over 1.0-3.0 V with 2032-coin cell after the cells were rested for 8 h.

[00142] *Cycling Results* – All solid-state Li/ $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) batteries were assembled with $\text{Li}_6\text{PS}_5\text{Cl}$ or $\text{Li}_6\text{PS}_5\text{Cl}\cdot\text{LiCl}$ as the respective solid electrolyte compositions, according to multiple embodiments and alternatives. Fig. 39 displays the cycling performance of Li/LTO cells at a C-rate of 0.2C within a voltage range of 1.0-3.0 V. In batteries, the discharge current is often expressed as a C-rate in order to normalize against battery capacity. A C-rate is a measure of the rate at which a battery is discharged relative to its maximum capacity. In comparison, the cell with LiCl rich solid electrolyte composition shows a higher specific capacity (135 mAh g^{-1}) than $\text{Li}_6\text{PS}_5\text{Cl}$ -based cell (110 mAh g^{-1}) after 50 cycles of charge/discharge, suggesting the positive role of excess Cl on the enhancement of electrochemical properties. The presence of lithium halide at the interface likely stabilizes the solid electrolyte composition/electrode interface and blocks side reactions. Accordingly, the improved cycling performance of the ASSB with $\text{Li}_6\text{PS}_5\text{Cl}\cdot\text{LiCl}$ as the solid electrolyte composition (as shown in Fig. 39) likely relates to the formation of a more stable solid electrolyte interphase layer due to the excess amount of Cl.

[00143] It will be understood that the embodiments described herein are not limited in their application to the details of the teachings and descriptions set forth, or as illustrated in the

accompanying figures. Rather, it will be understood that the present embodiments and alternatives, as described and claimed herein, are capable of being practiced or carried out in various ways. Also, it is to be understood that words and phrases used herein are for the purpose of description and should not be regarded as limiting. The use herein of “including,” “comprising,” “e.g.,” “containing,” or “having” and variations of those words is meant to encompass the items listed thereafter, and equivalents of those, as well as additional items.

[00144] Accordingly, the foregoing descriptions of several embodiments and alternatives are meant to illustrate, rather than to serve as limits on the scope of what has been disclosed herein. The descriptions herein are not intended to be exhaustive, nor are they meant to limit the understanding of the embodiments to the precise forms disclosed. It will be understood by those having ordinary skill in the art that modifications and variations of these embodiments are reasonably possible in light of the above teachings and descriptions.

CLAIMS

What is claimed is:

1. An electrochemical energy storage device comprising a solid electrolyte composition, wherein the solid electrolyte composition comprises a solid, halide-containing crystalline lithium argyrodite characterized by an ionic conductivity of at least 0.1 mS cm^{-1} at about 22°C , wherein a molar ratio of sulfur to halide is in a range of 1.5:1 - 5:1.
2. The electrochemical energy storage device of claim 1, wherein the molar ratio of sulfur to halide is at least 2.5:1.
3. The solid electrolyte composition of claim 1, wherein the solid, halide-containing crystalline lithium argyrodite is characterized by an ionic conductivity in the range of 0.1 mS cm^{-1} to 0.5 mS cm^{-1} at about 22°C .
4. The solid electrolyte composition of claim 1, wherein the solid, halide-containing crystalline lithium argyrodite is characterized by an ionic conductivity of at least 1.5 mS cm^{-1} at 90°C .
5. The electrochemical energy storage device of claim 1, wherein the device is an all-solid state battery.
6. The electrochemical energy storage device of claim 5, wherein the device when cycling at a C-rate of 0.2C is characterized by a specific capacity greater than 110 mAh g^{-1} after 50 cycles of charge/discharge.

7. A method for synthesizing lithium argyrodites, comprising:
dissolving a mixture of precursors in a solvent;
drying the mixture above about 22° C in a chamber by flowing an inert gas into the chamber or applying a vacuum within the chamber to yield a precipitate; and
annealing the precipitate at a temperature higher than 150° C under vacuum or the inert gas atmosphere to yield a lithium compound having an argyrodite crystal structure.
8. The method of claim 7, wherein the drying and annealing steps are performed in about 2 hours or less.
9. The method of claim 7, wherein the lithium compound having an argyrodite crystal structure exhibits an ionic conductivity in the range of 0.1 mS cm⁻¹ to 0.6 mS cm⁻¹ at about 22° C.
10. The method of claim 7, wherein the lithium compound having an argyrodite crystal structure exhibits an ionic conductivity of at least 1.5 mS cm⁻¹ at 90° C.
11. The method of claim 7, wherein the precursors comprise Li₂S combined with one of Li₃PS₄, Li₃PS₄-ACN, or Li₃PS₄-THF.
12. The method of claim 7, wherein the precursors comprise Li₃PS₄, Li₂S, and LiX, where X represents at least one halide or a combination of halides.

13. The method of claim 7, wherein the lithium compound having an argyrodite crystal structure is characterized by an XRD pattern having a peak at 26 ± 1 degree, a second peak at about 30 degrees, and a third peak at about 31 degrees.
14. The method of claim 7, wherein the lithium compound having an argyrodite crystal structure is represented by a formula chosen from the group consisting of $\text{Li}_m\text{PS}_n\text{X}_o$ and Li_mPS_n , where m is a number in the range of 4-8, n is a number in the range of 3-6, X represents at least one halide, and o is a number in the range of 0-3.
15. The method of claim 7, wherein the lithium compound having an argyrodite crystal structure has a chloride content expressed as $\text{Li}_6\text{PS}_5\text{Cl} \cdot x\text{LiCl}$ wherein x is between 0-2.

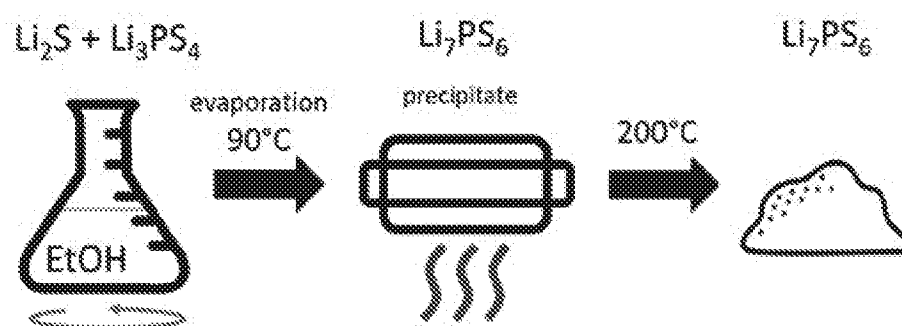


Figure 1

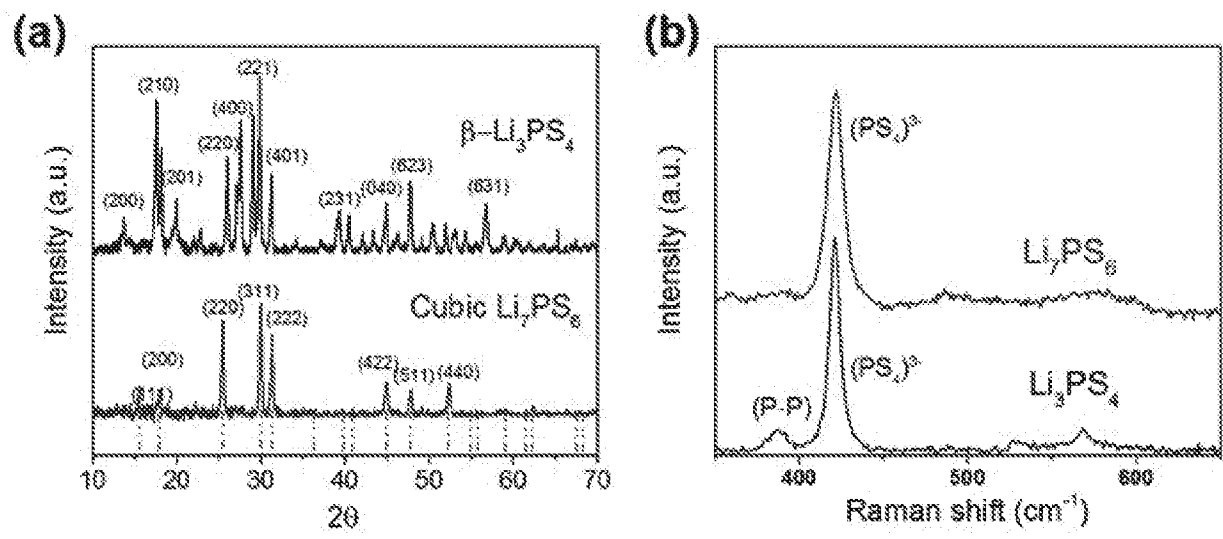


Figure 2

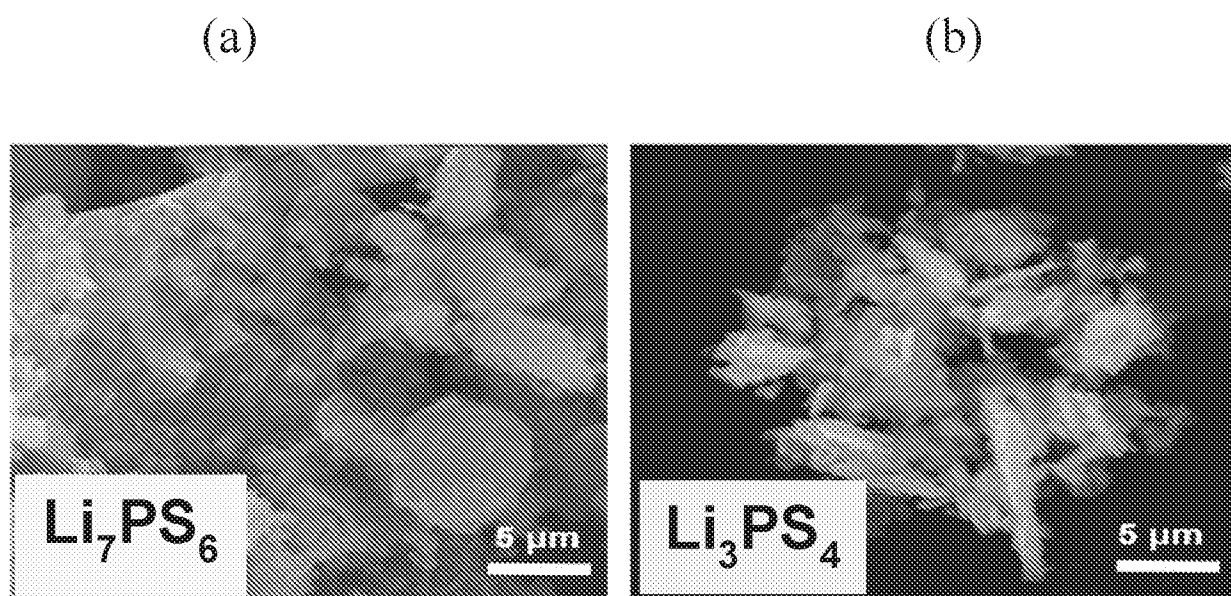


Figure 3

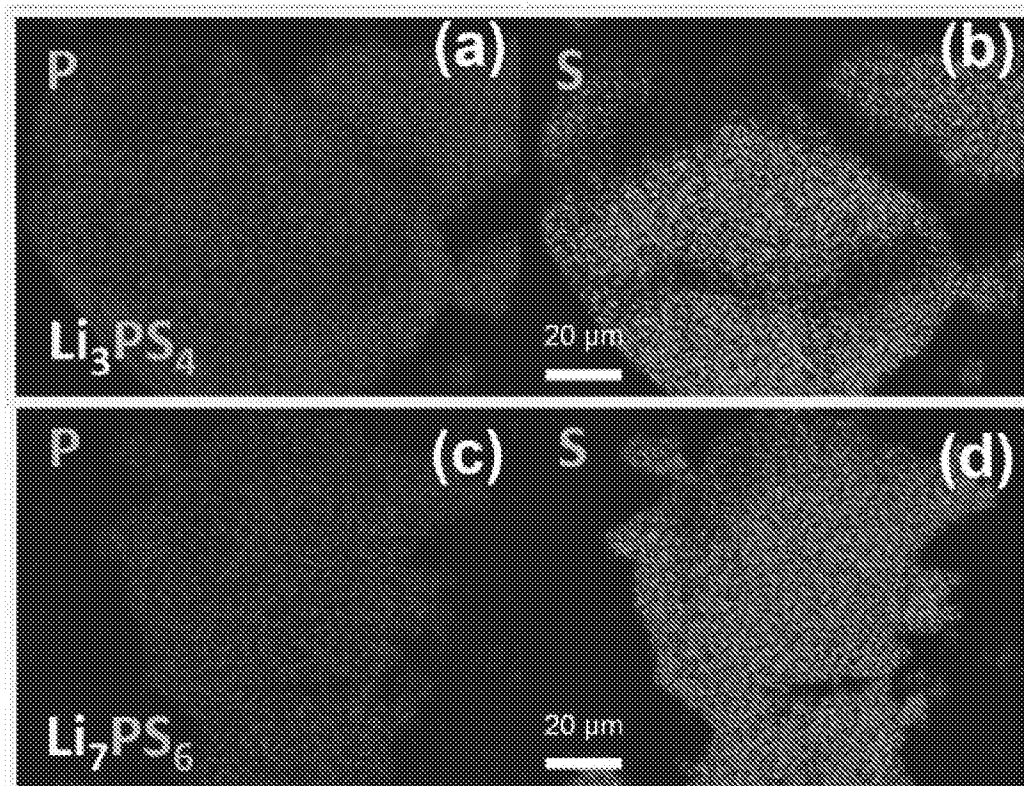


Figure 4

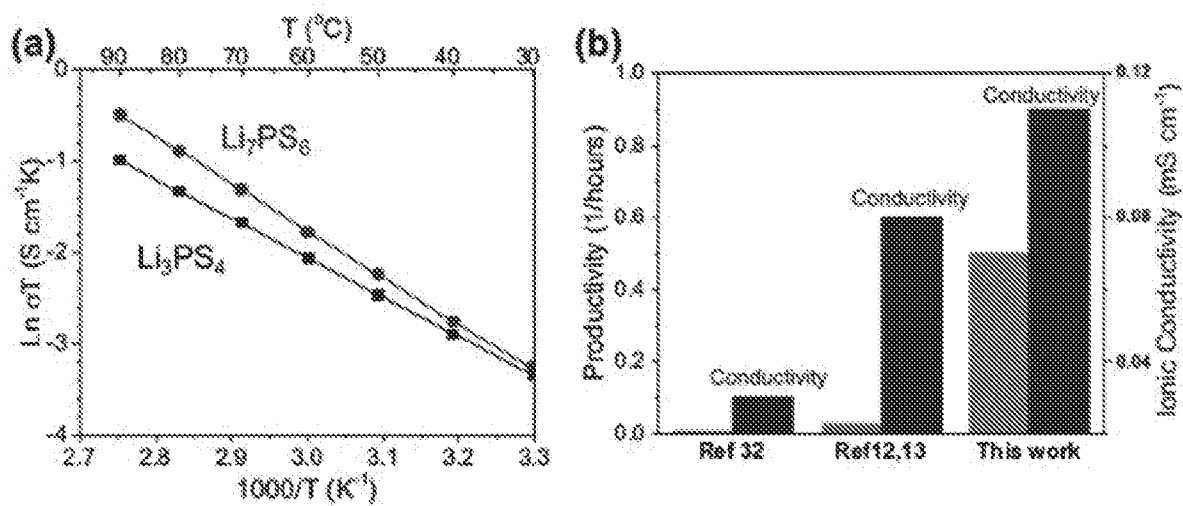


Figure 5

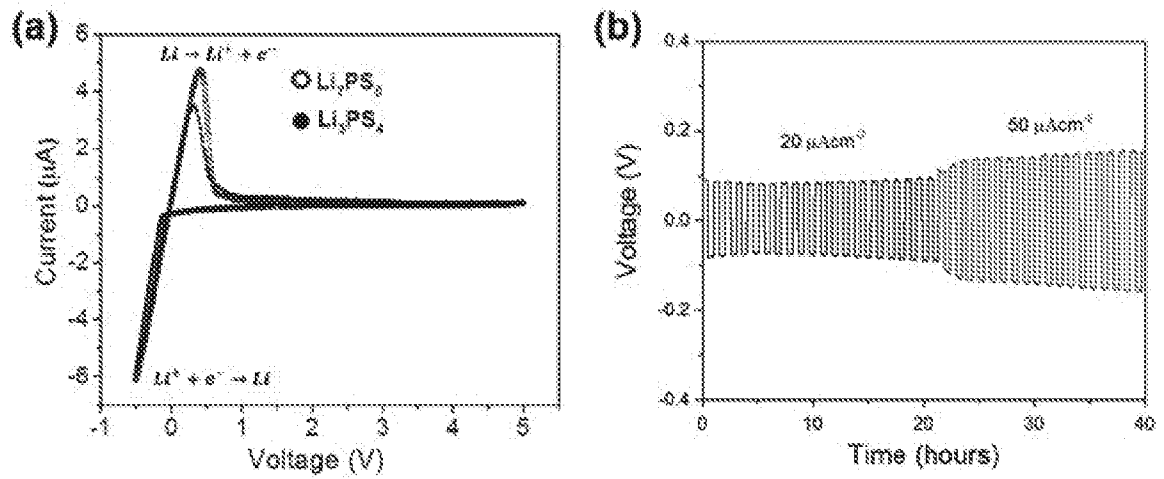


Figure 6

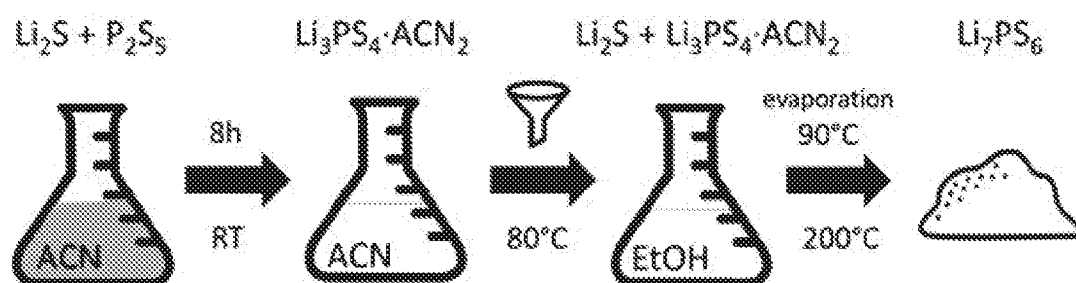


Figure 7

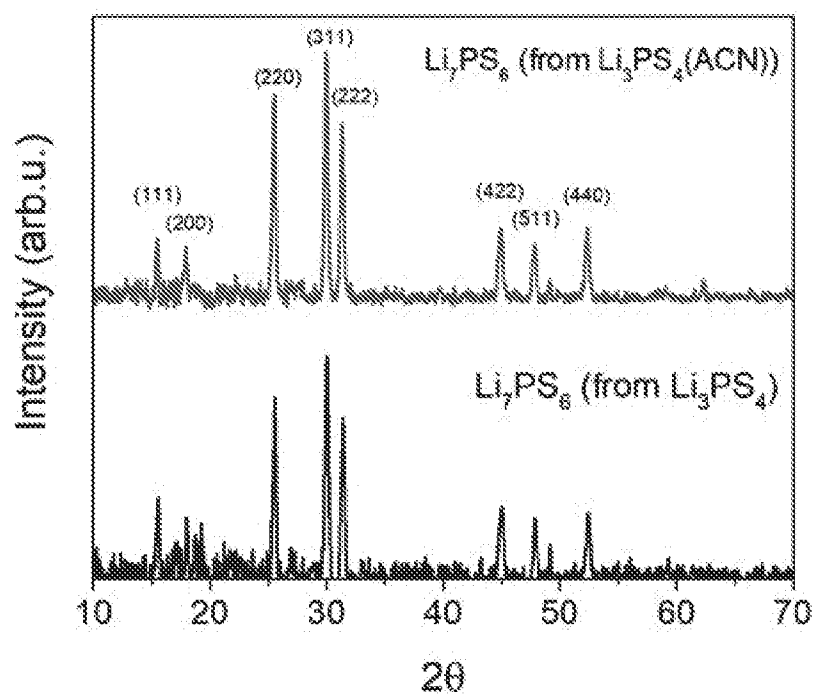


Figure 8

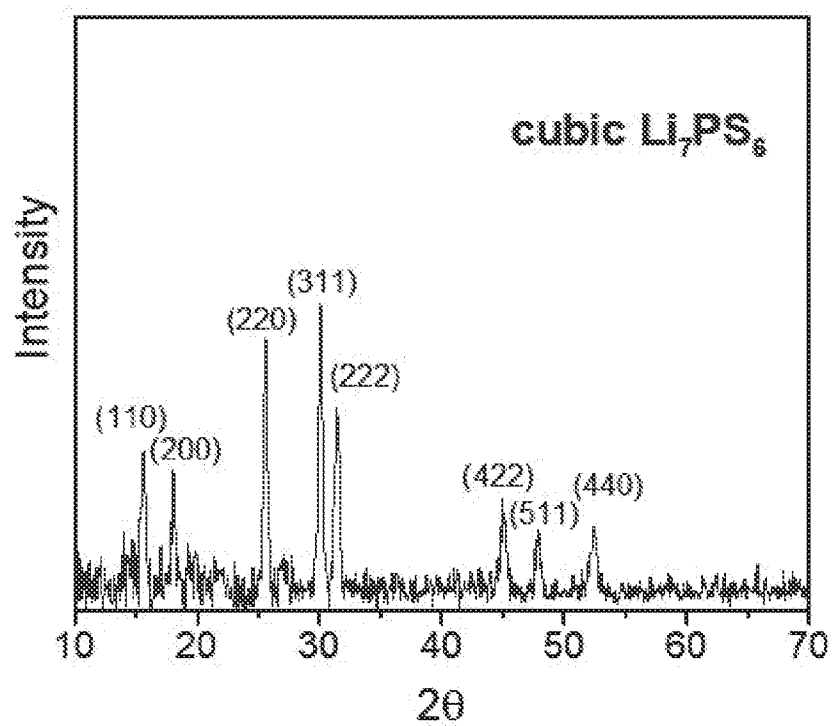


Figure 9

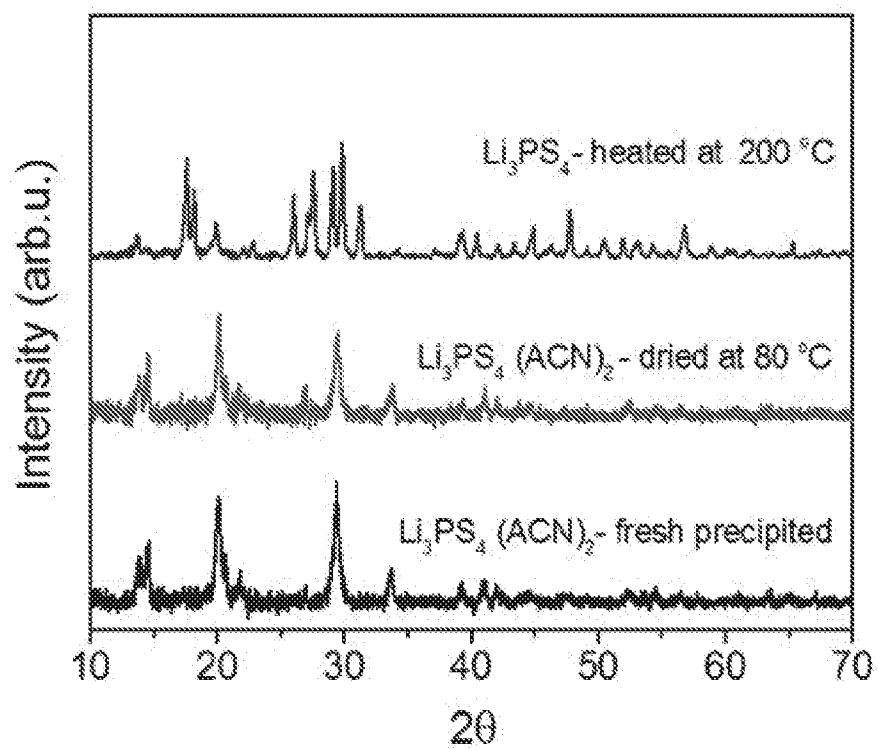


Figure 10

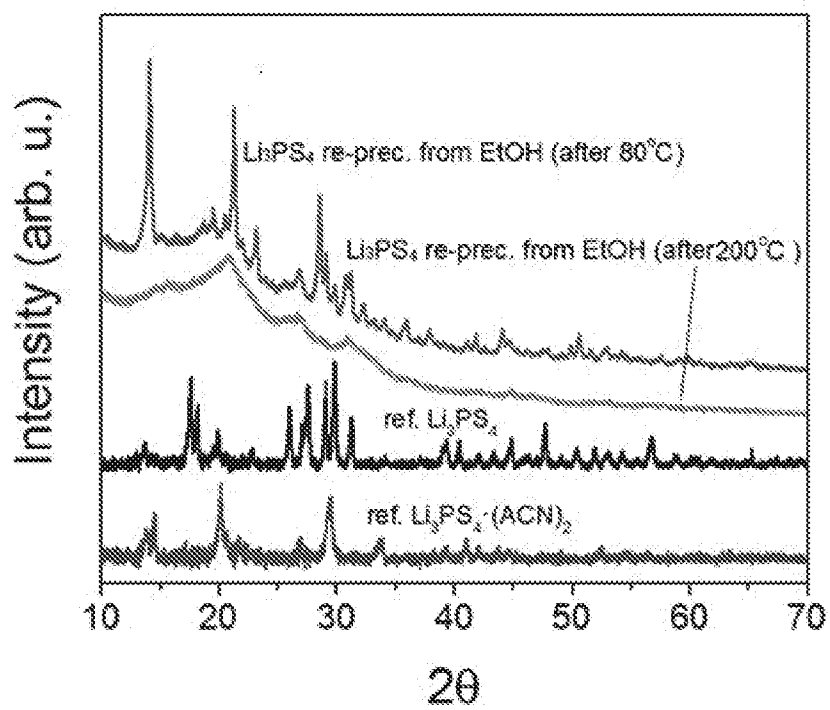


Figure 11

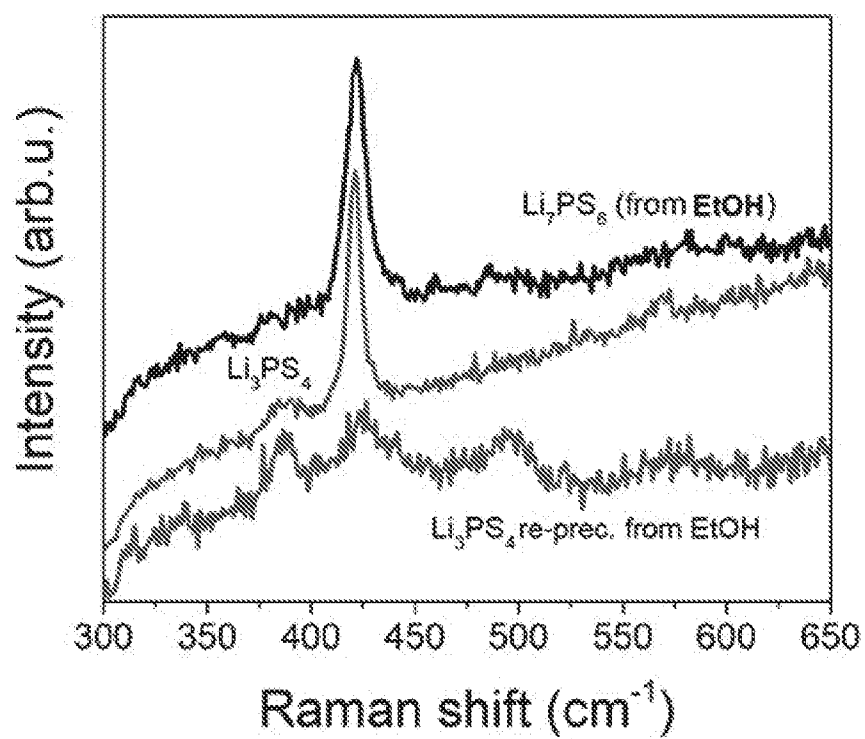


Figure 12

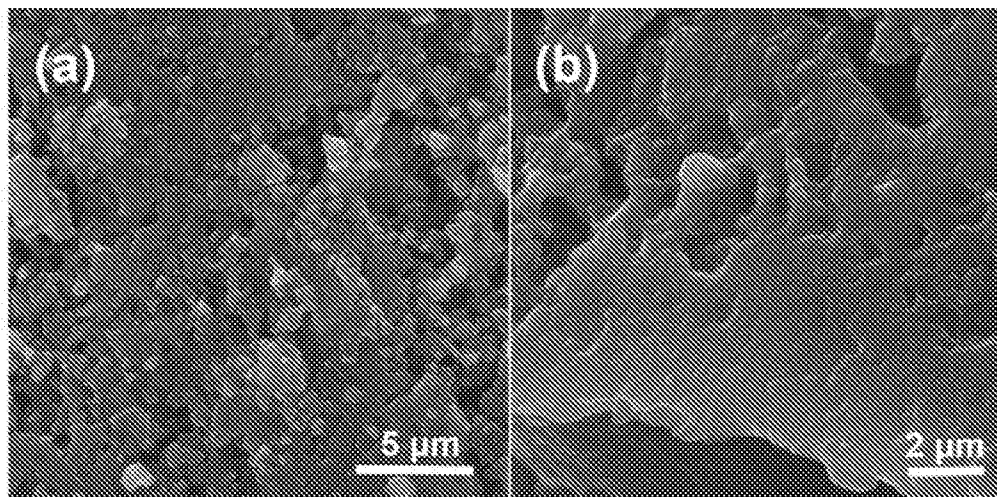


Figure 13

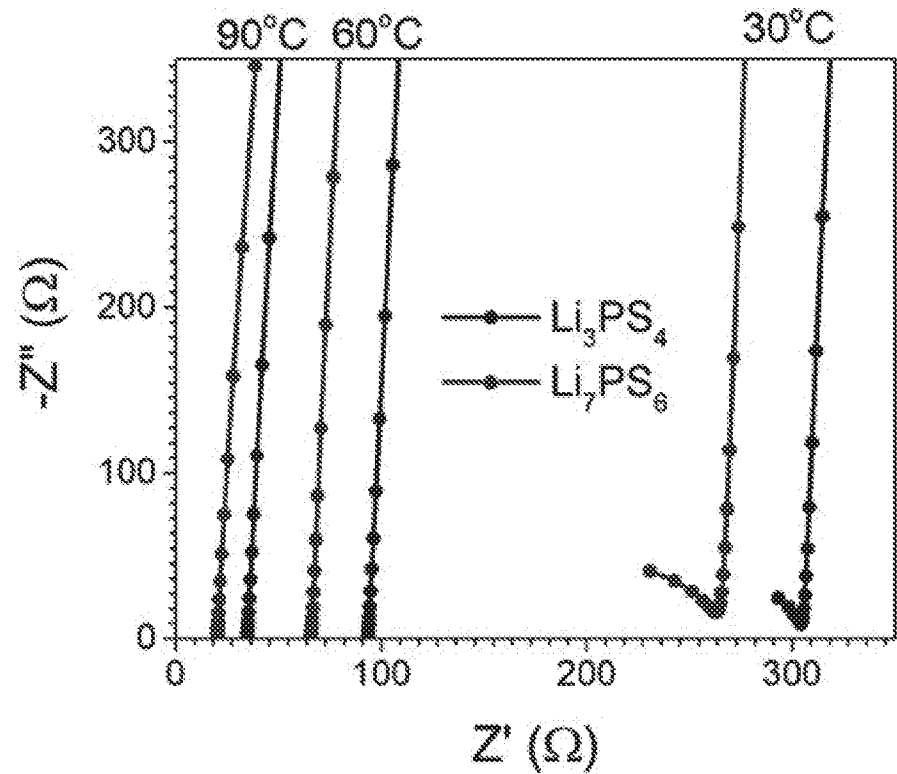


Figure 14

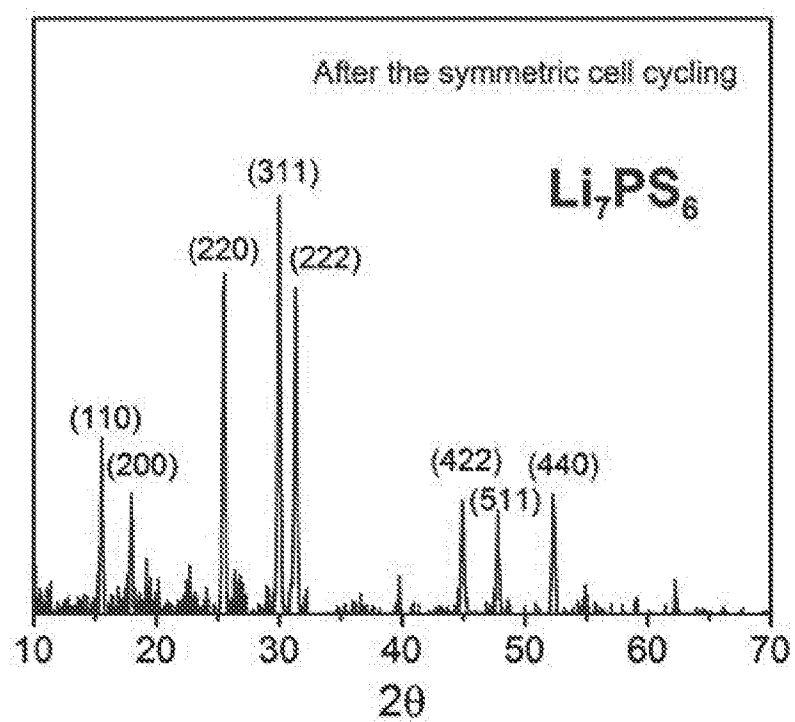


Figure 15

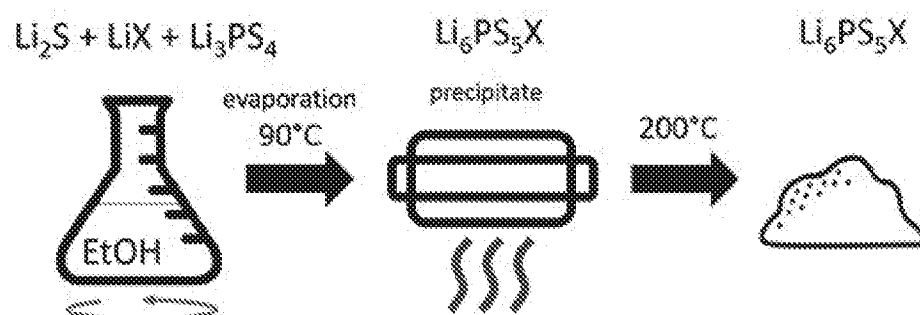


Figure 16

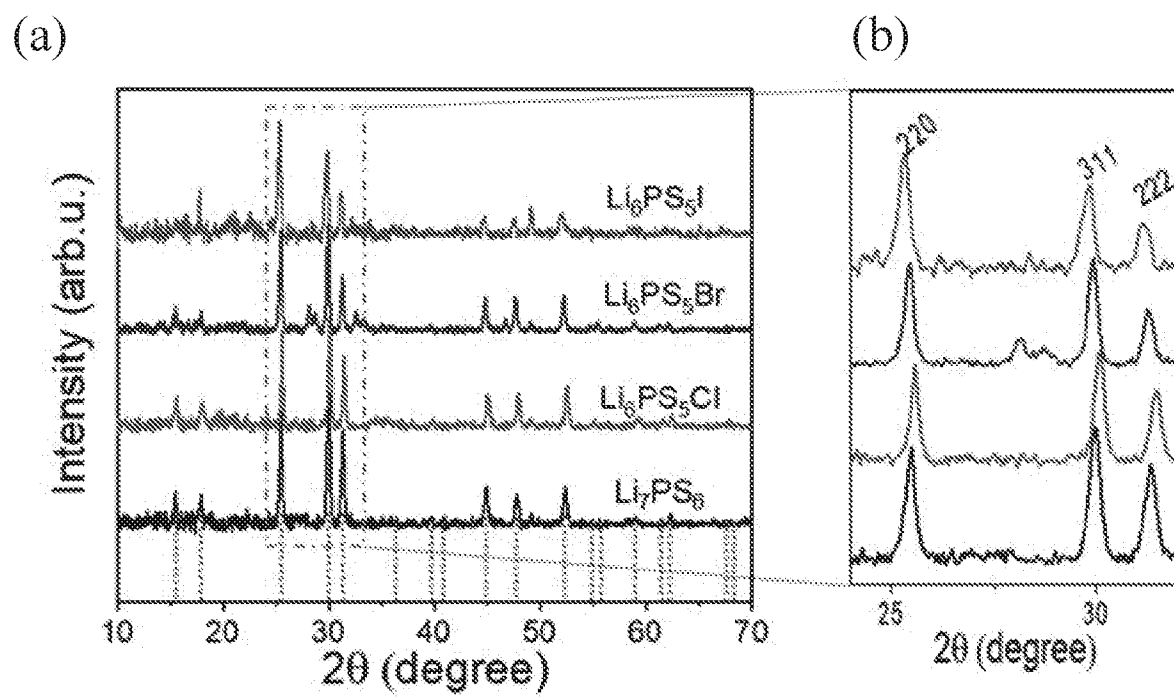


Figure 17

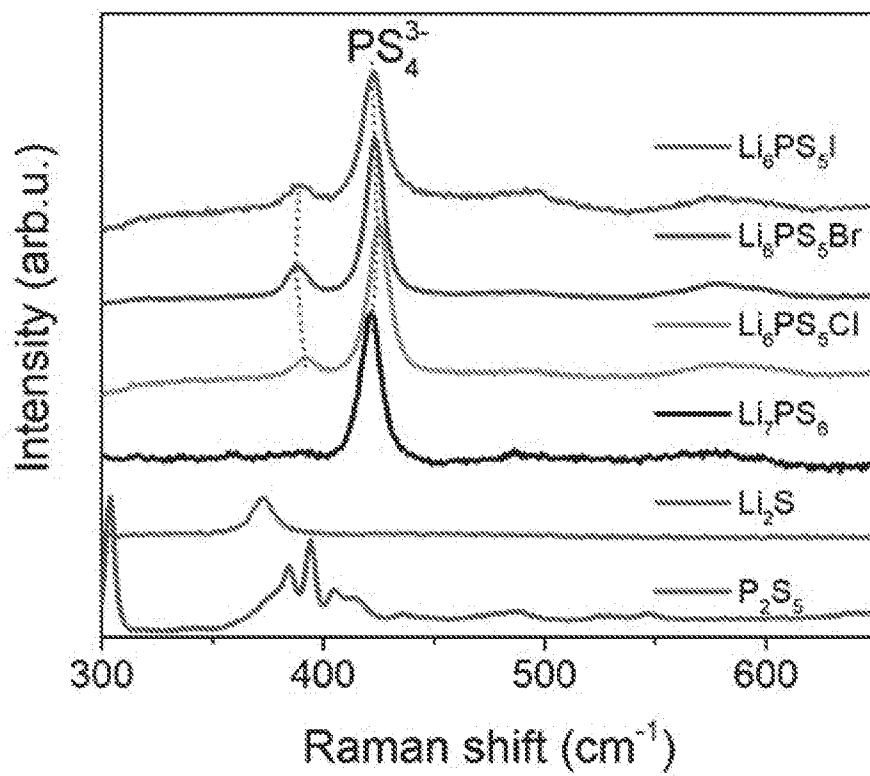


Figure 18

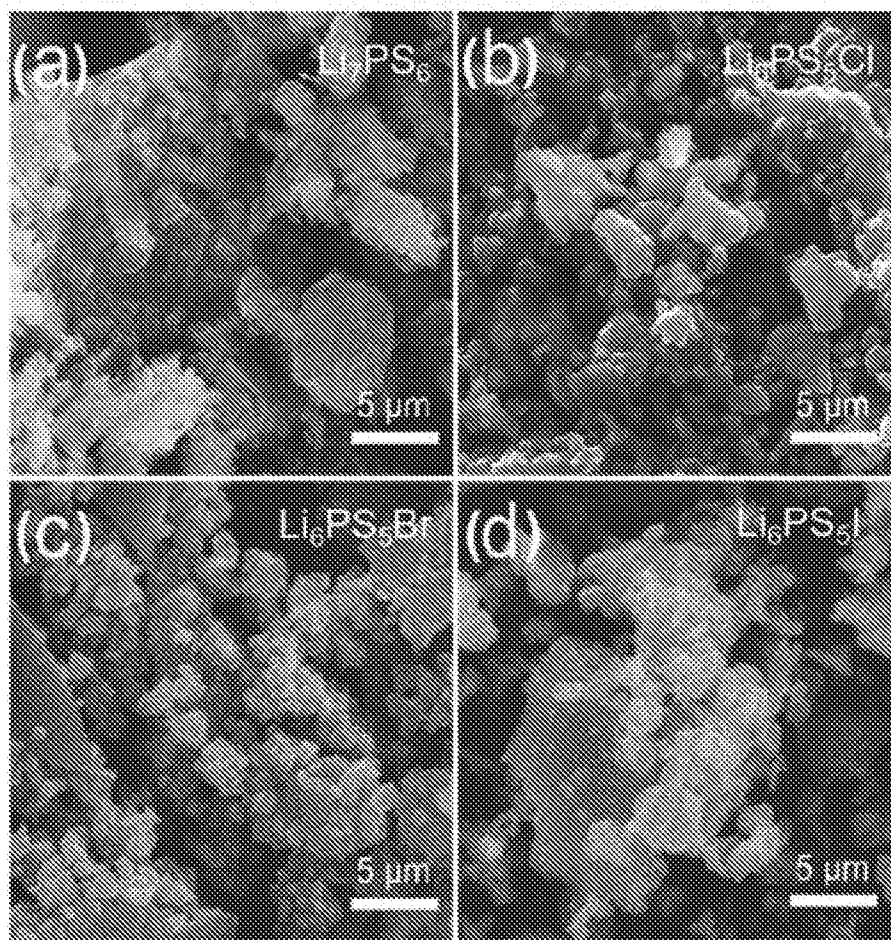


Figure 19

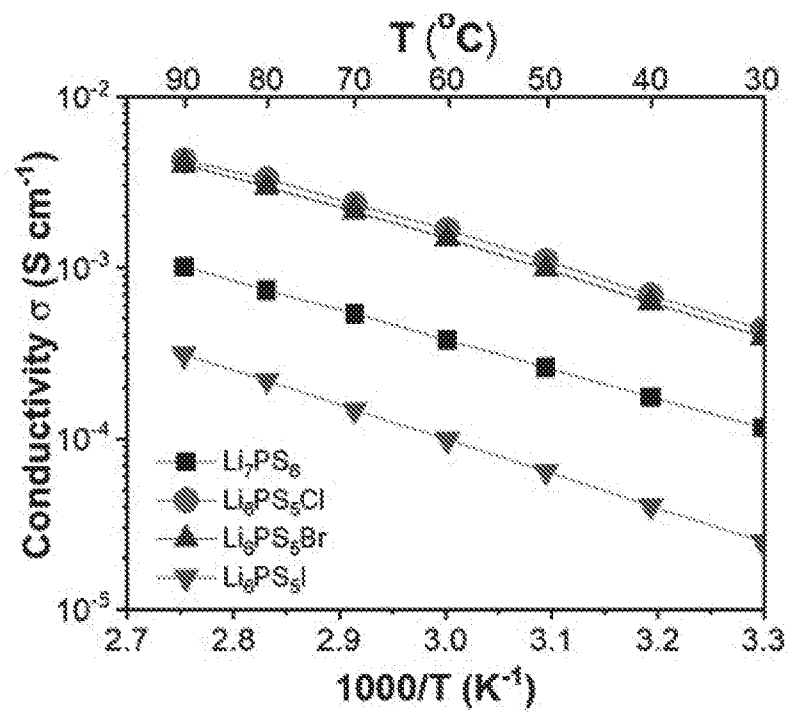


Figure 20

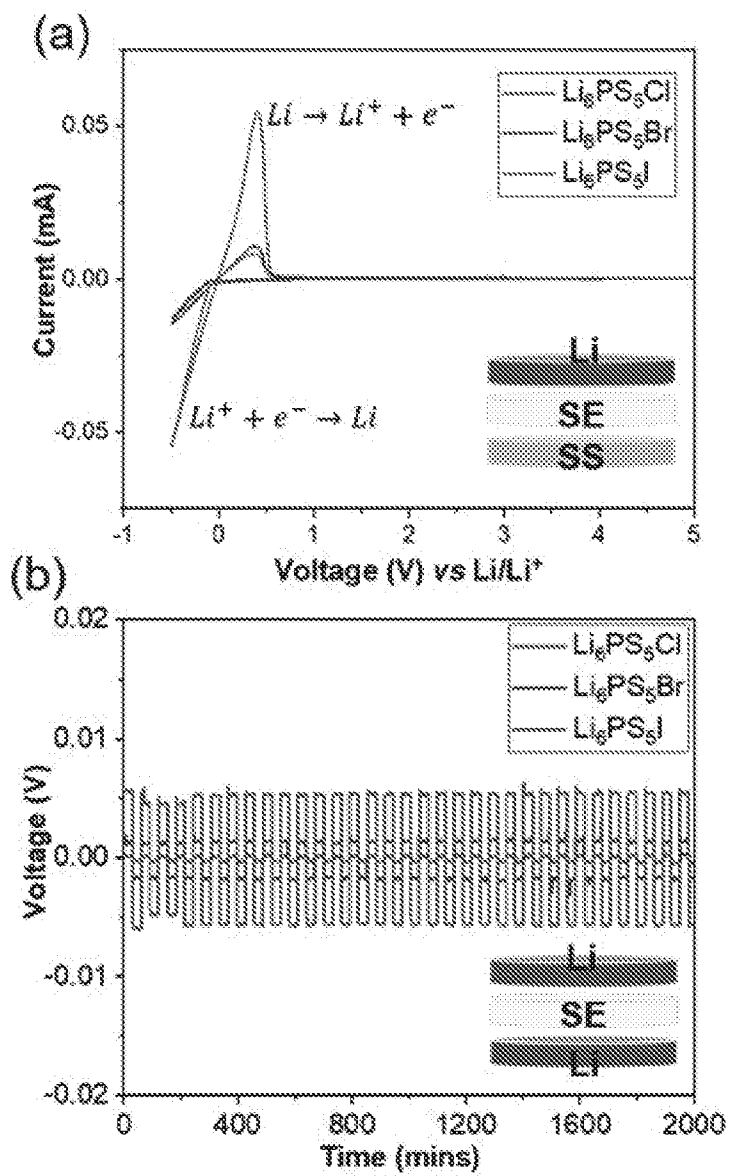


Figure 21

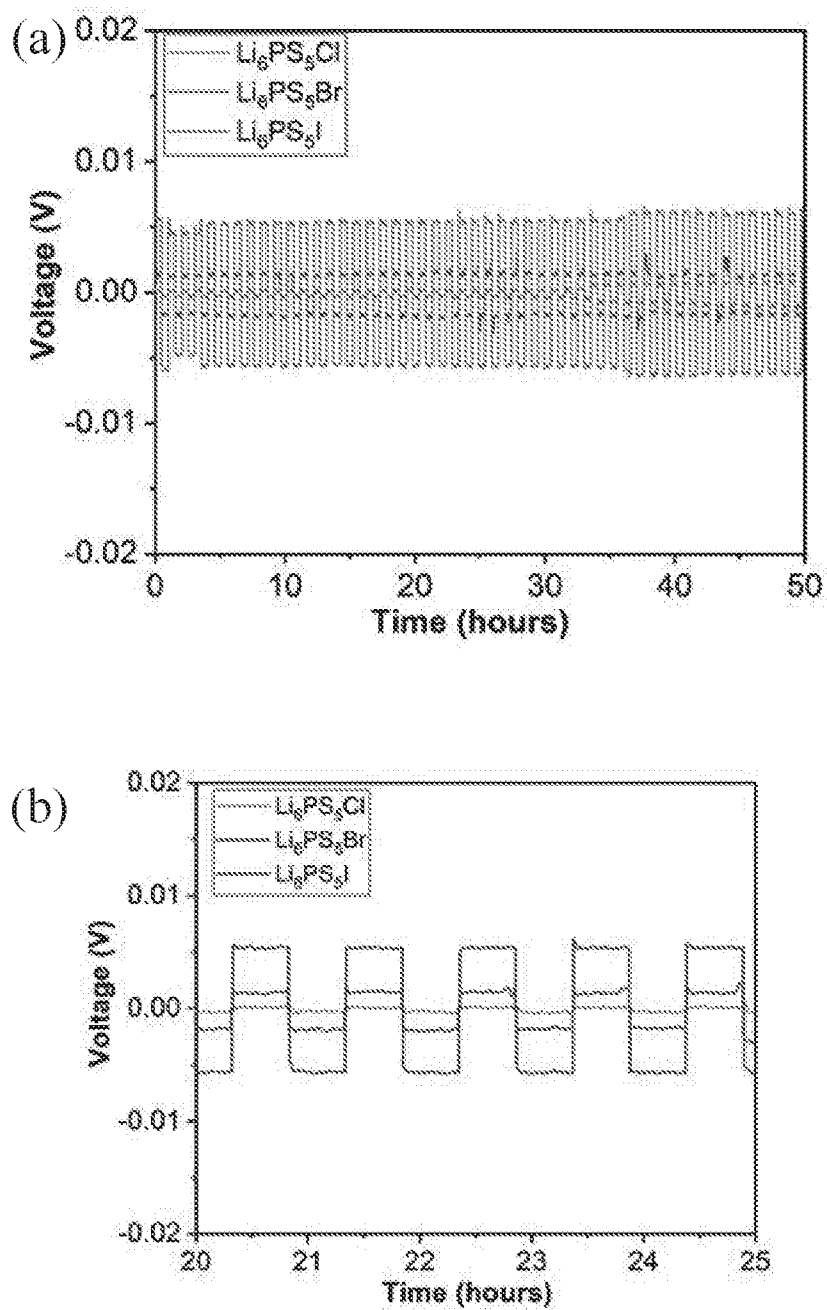


Figure 22

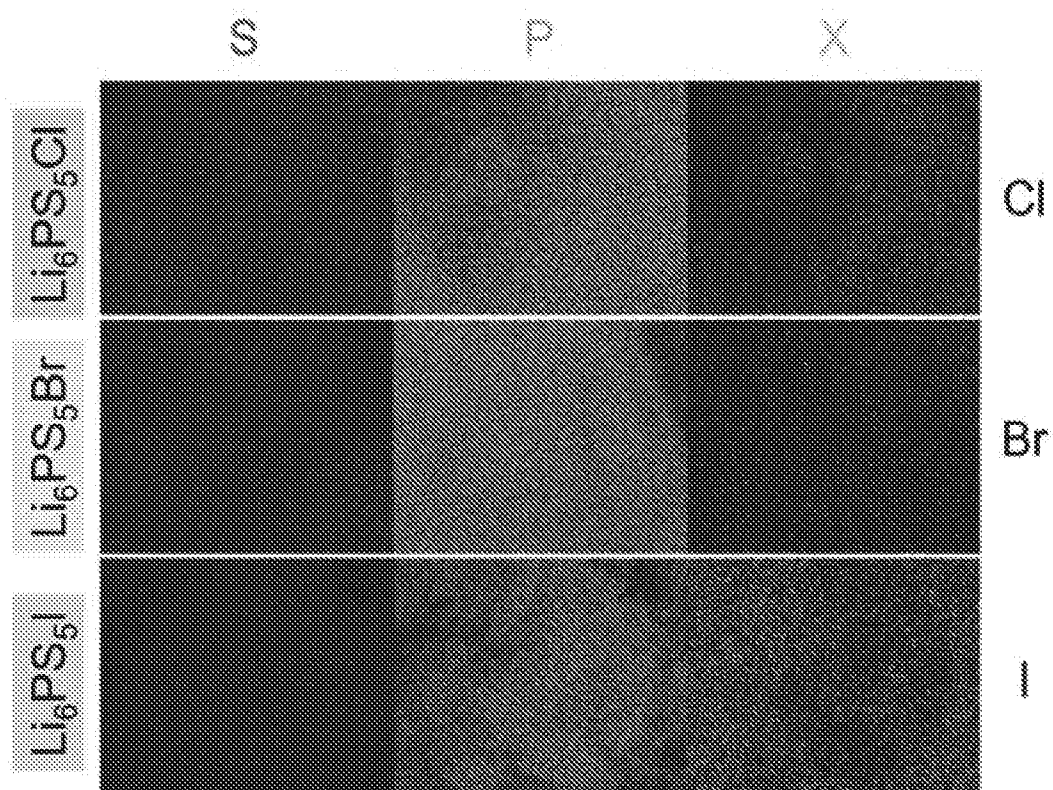


Figure 23

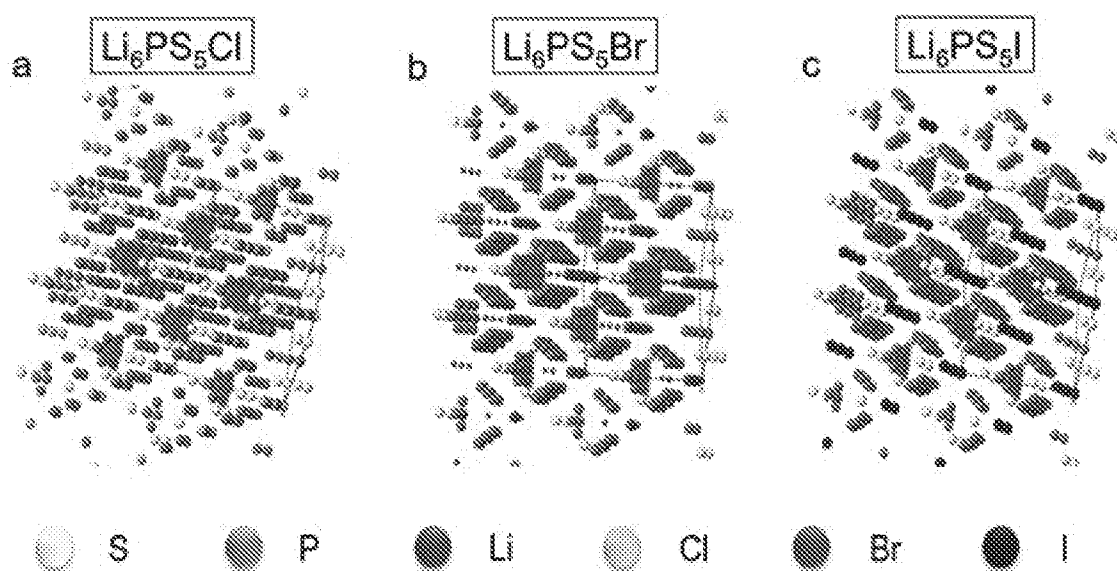


Figure 24

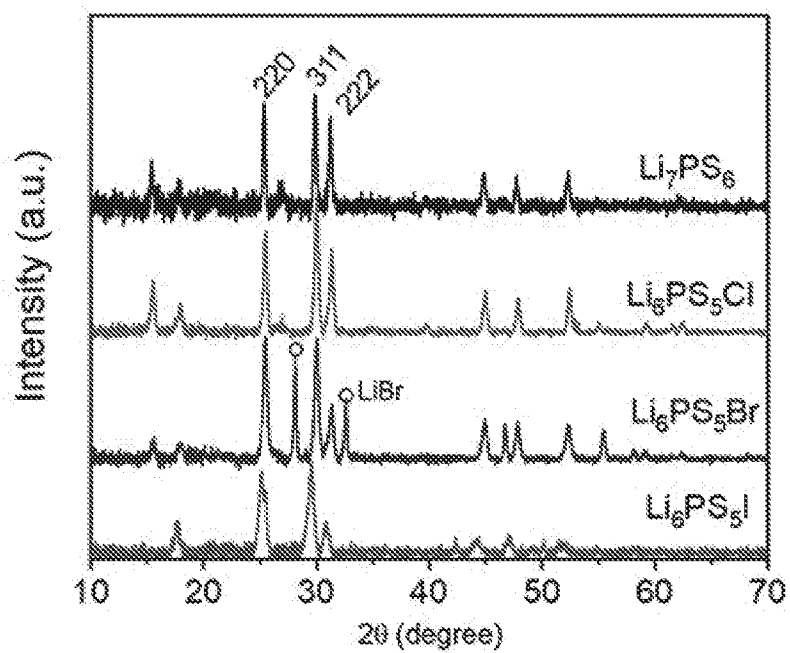


Figure 25

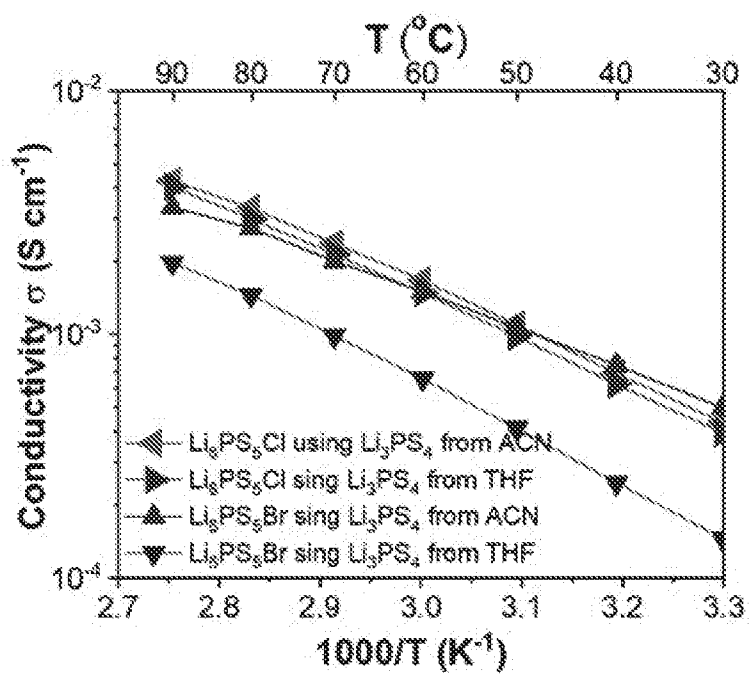


Figure 26

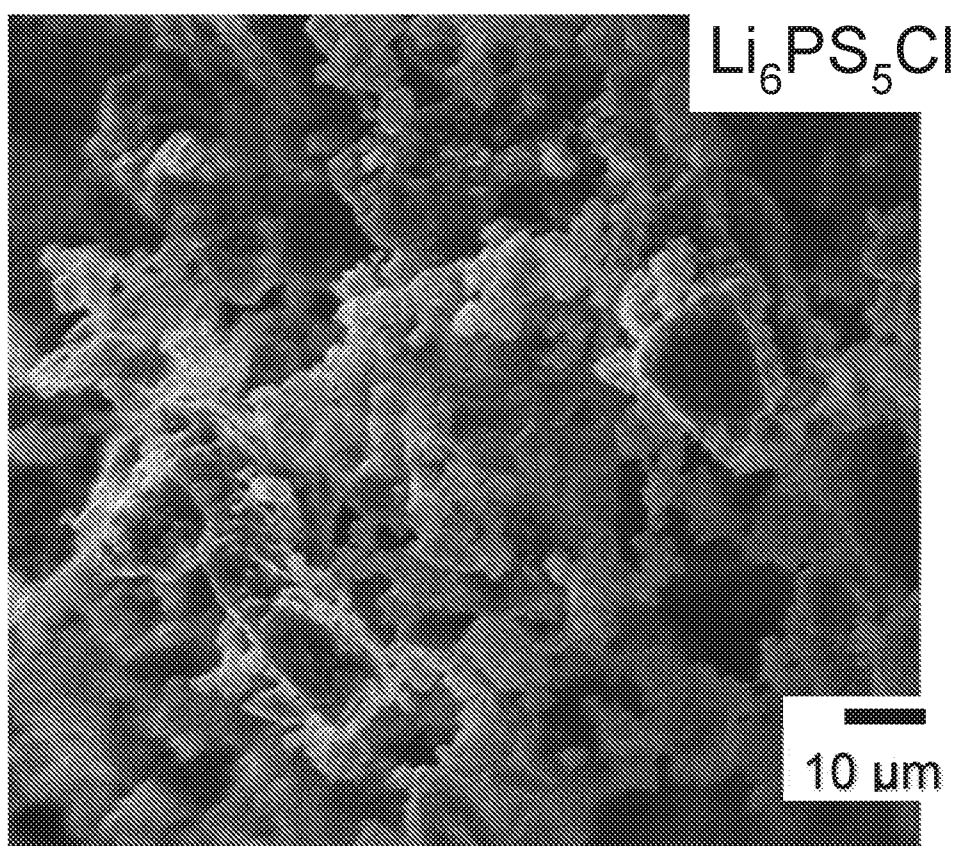


Figure 27

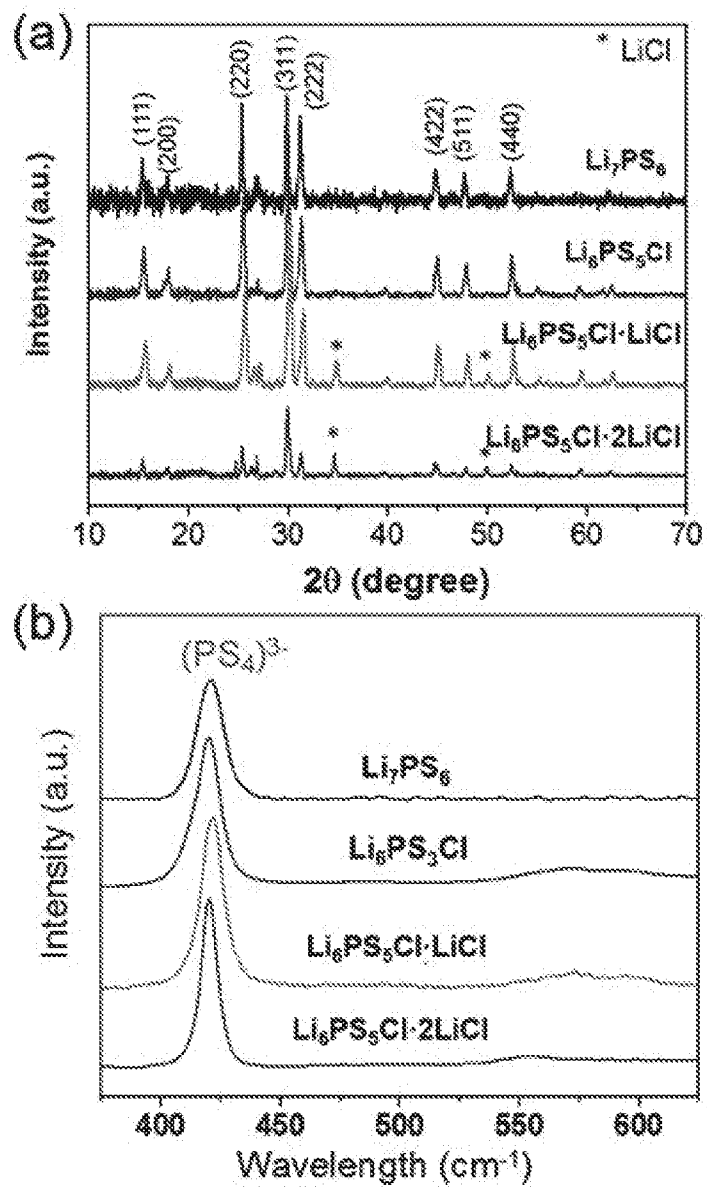


Figure 28

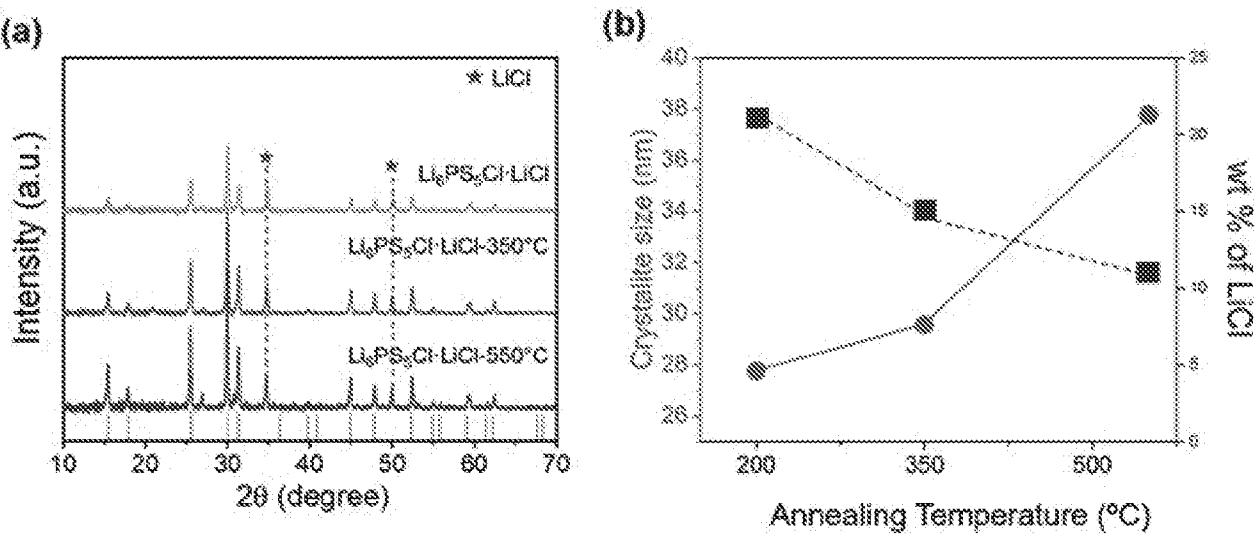


Figure 29

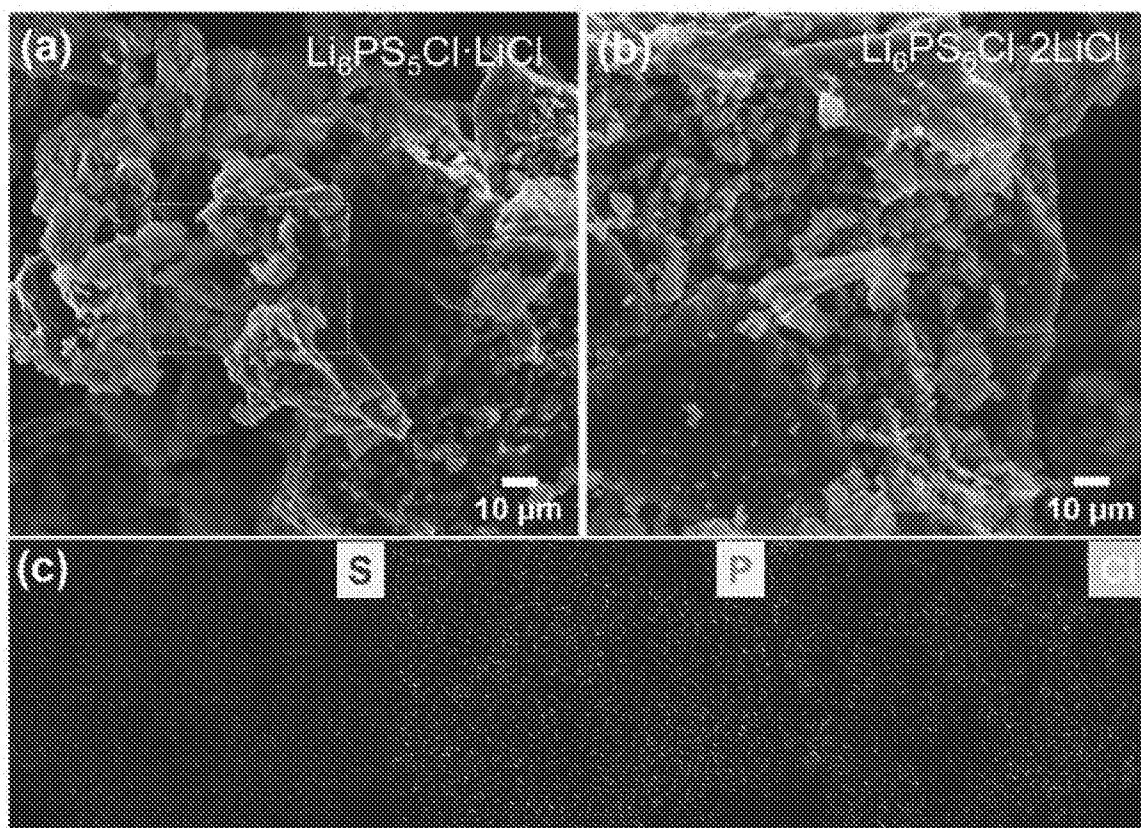


Figure 30

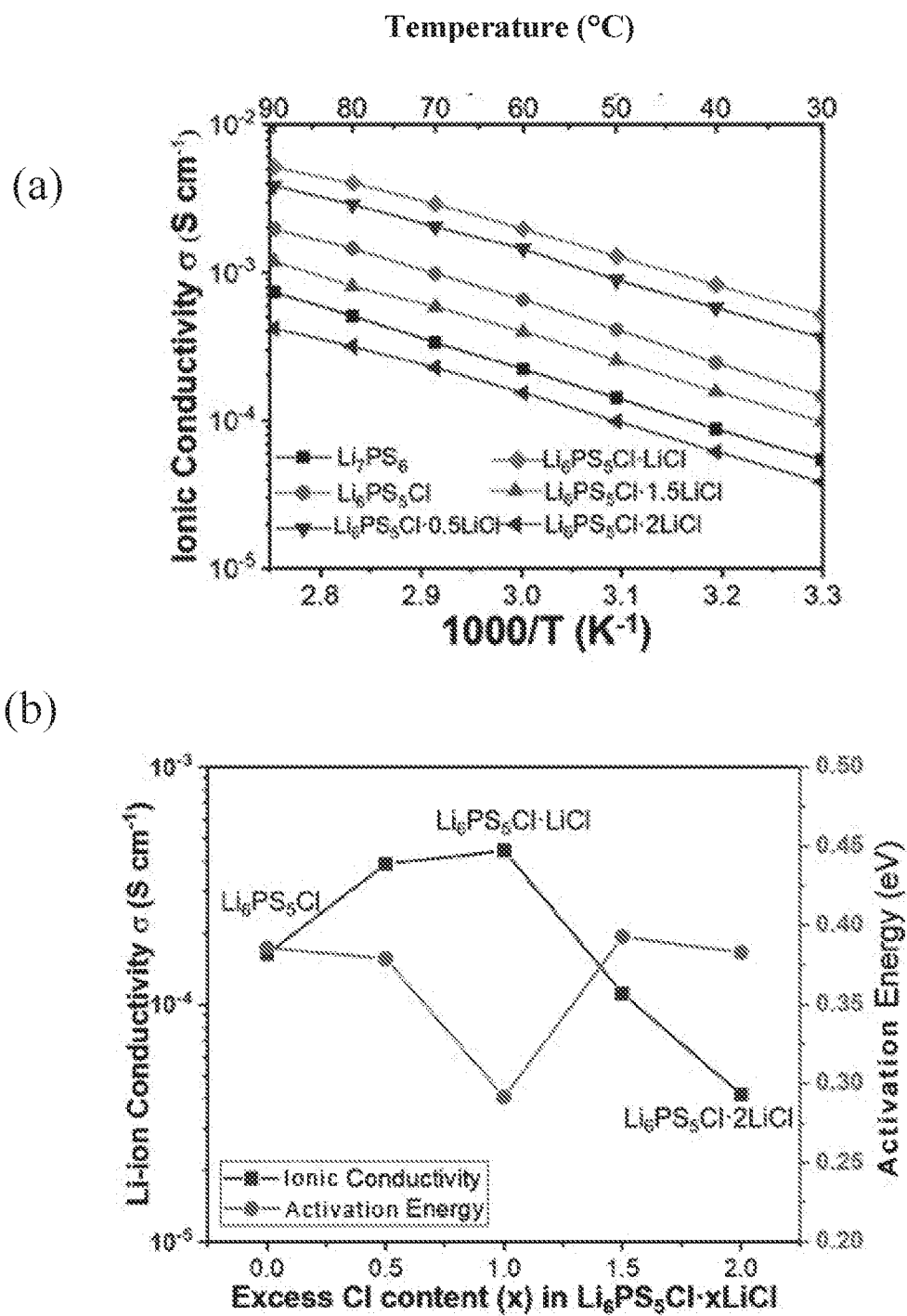


Figure 31

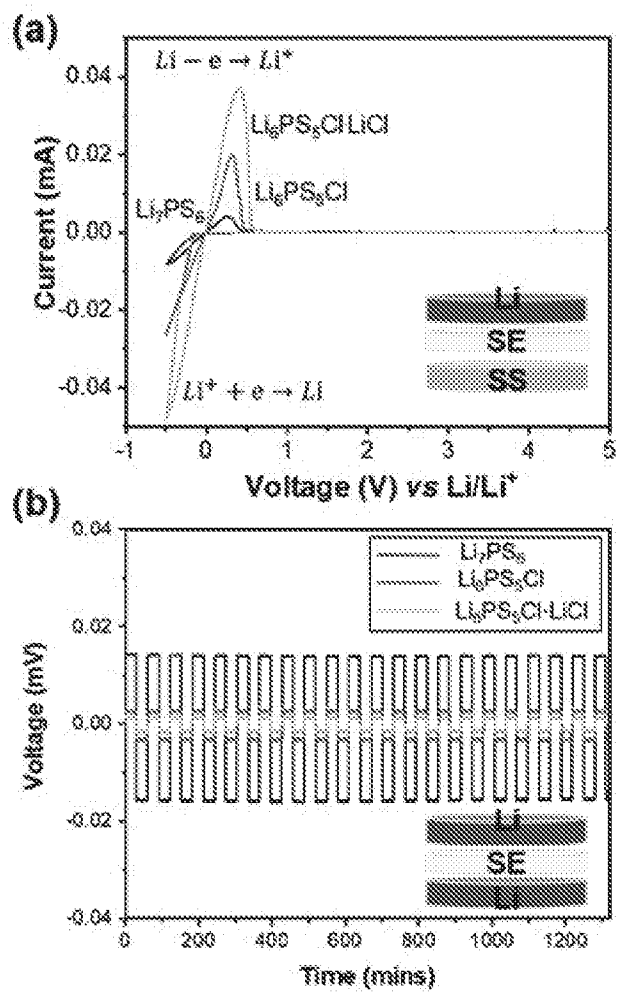


Figure 32

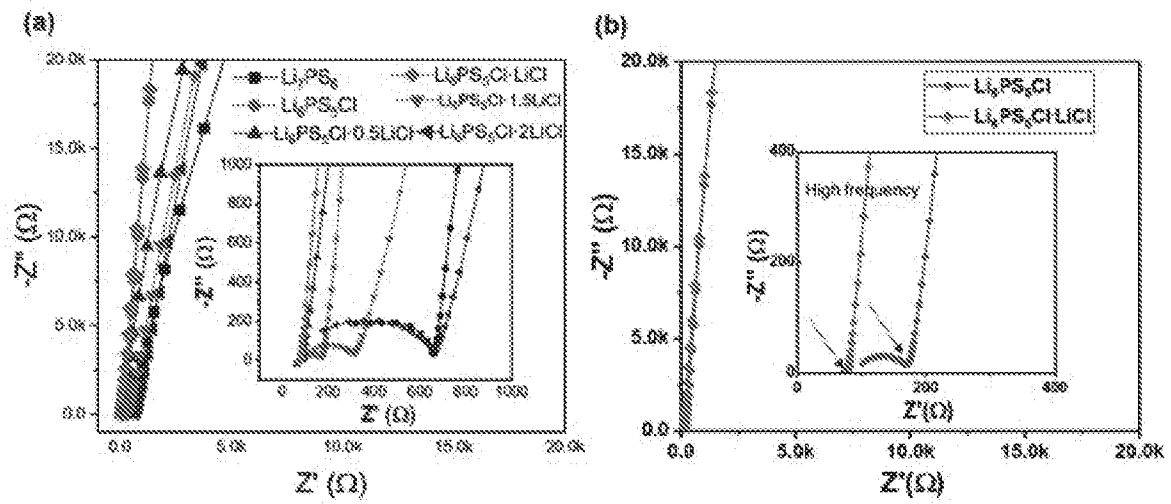


Figure 33

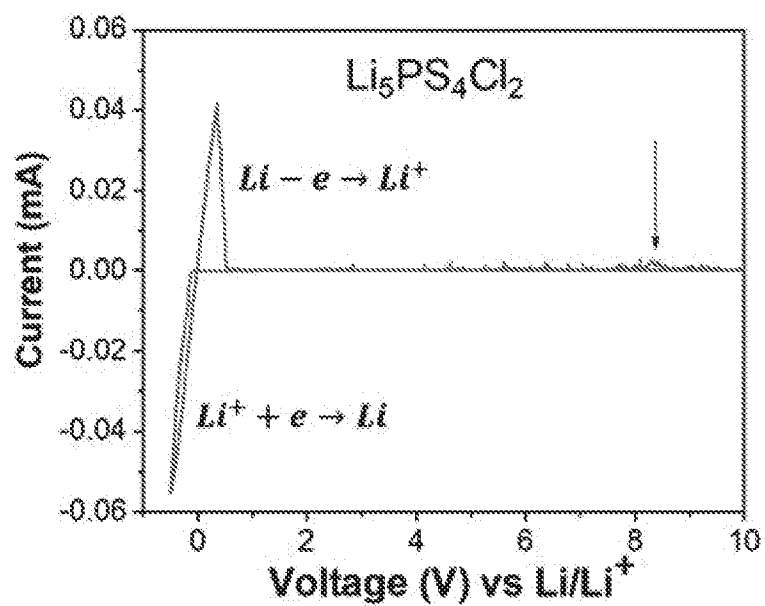


Figure 34

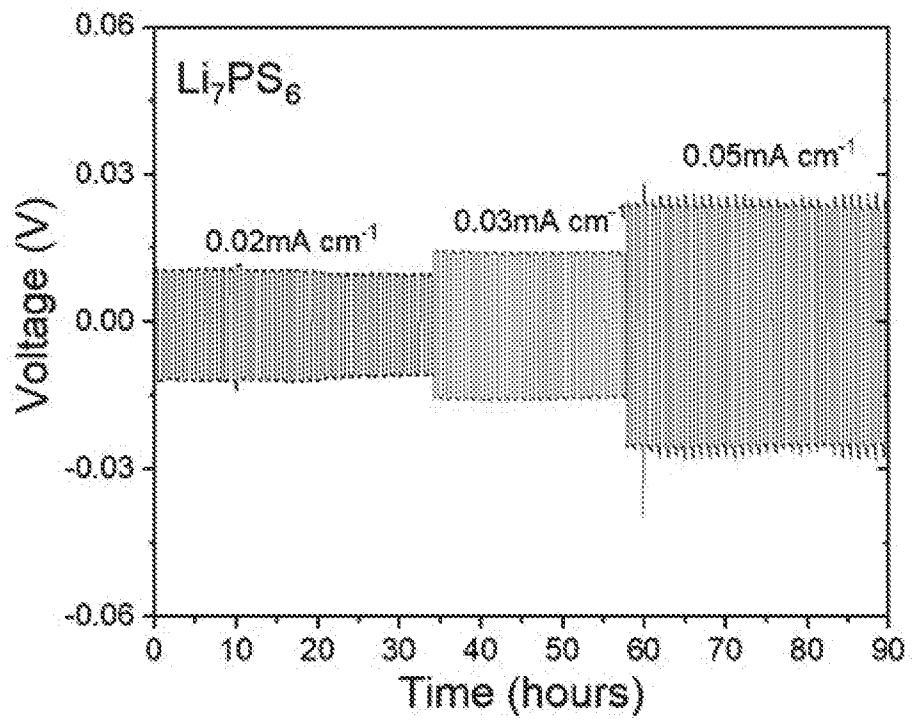


Figure 35

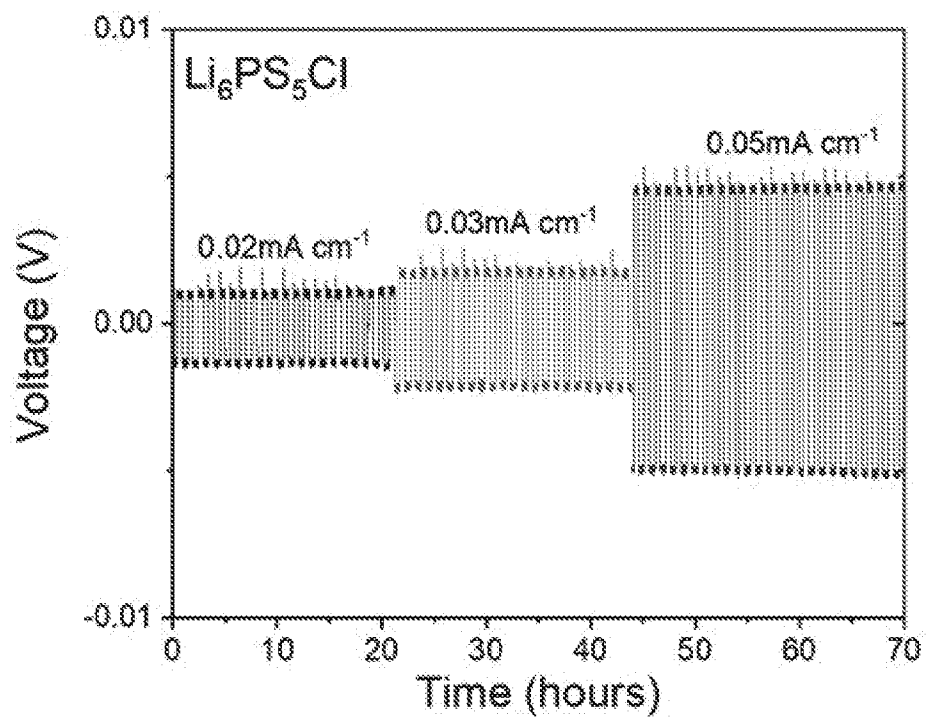


Figure 36

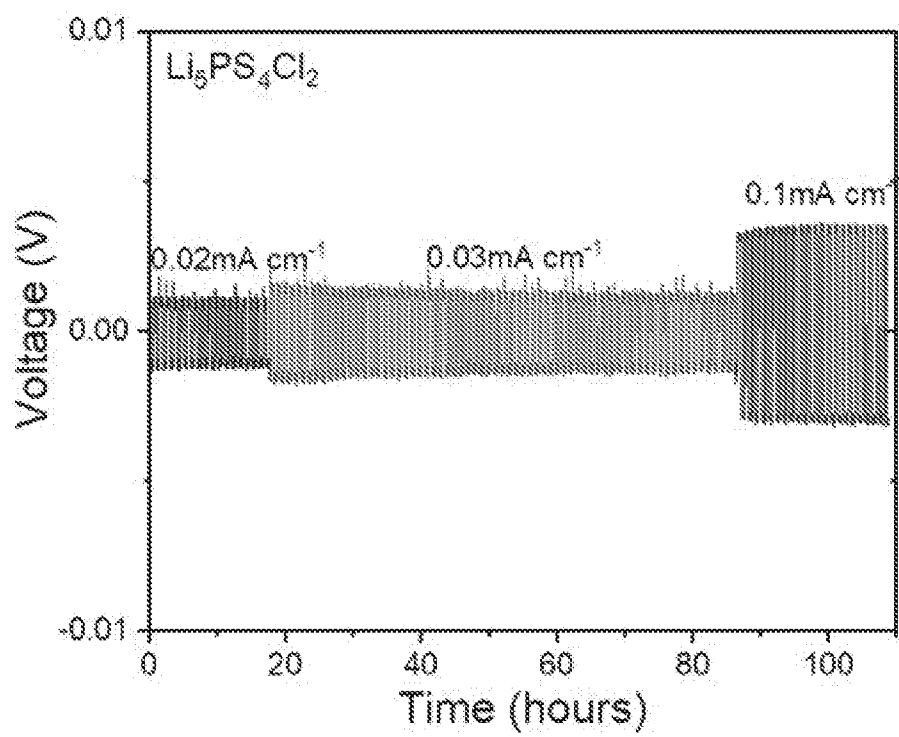


Figure 37

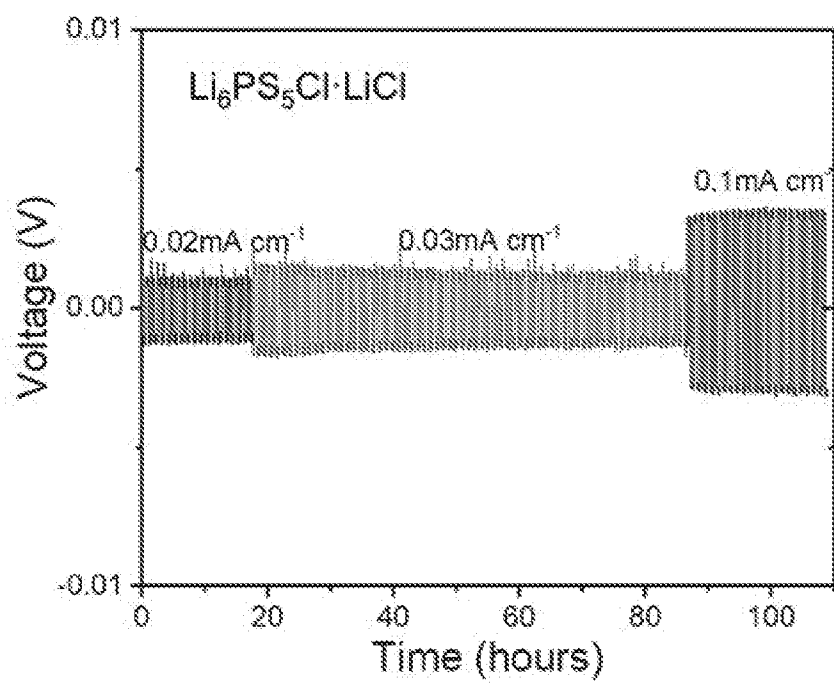


Figure 38

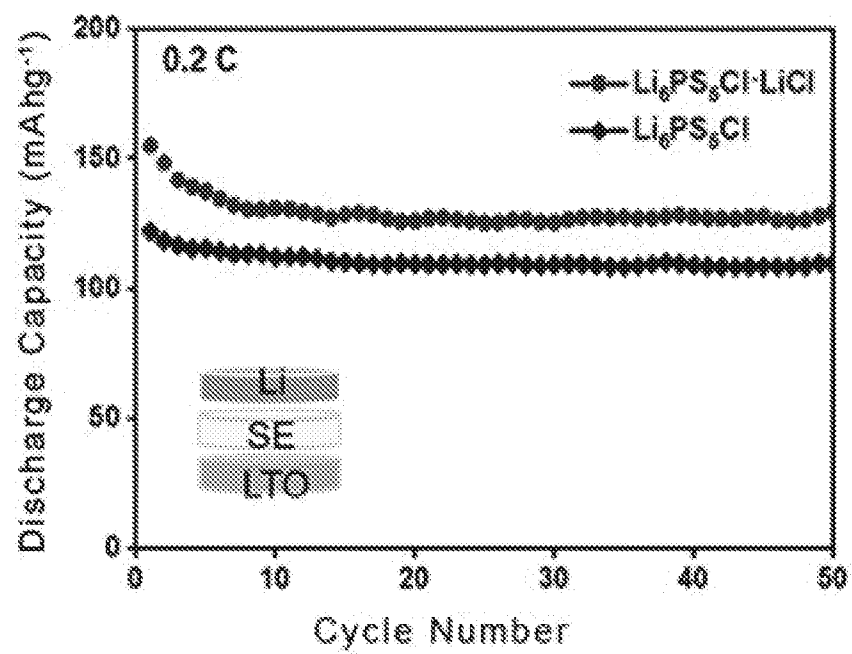


Figure 39

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/28471

A. CLASSIFICATION OF SUBJECT MATTER

IPC - C01D 15/00, H01M 10/0562 (2020.01)

CPC - C01D 15/00, H01M 10/0562, H01M 6/185, H01M 6/188, H01M 10/02, H01M 2300/0068, H01M 2300/008

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	WANG, Heng, et al. "A lithium argyrodite Li6PS5Cl0.5Br0.5 electrolyte with improved bulk and interfacial conductivity." Journal of Power Sources 412 (2019): 29-36, Available online 29 November 2018 (29.11.2018), abstract; pg 29, 30, 35 [online] < https://www.researchgate.net/profile/Chuang_Yu3/publication/329277420_A_lithium_argyrodite_Li_6_PS_5_Cl_05_Br_05_electrolyte_with_improved_bulk_and_interfacial_conductivity/links/5c000e80a6fdcc1b8d4a7cb0/A-lithium-argyrodite-Li-6-PS-5-Cl-05-Br-05-electrolyte-with-improved-bulk-and-interfacial-conductivity.pdf >	1-5 ----- 6
X	US 2010/0290969 A1 (DEISEROTH et al.) 18 November 2010 (18.11.2010), para [0006], [0010], [0032]	1, 2
Y	CHEN, Maohua, et al. "All-solid-state MoS 2/Li6PS5Br/In-Li batteries as a novel type of Li/S battery." Journal of Materials Chemistry A 3.20 (2015): 10698-10702, pg 1 [online] < https://pubs.rsc.org/en/content/getauthorversionpdf/c5ta02372f >	6

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"D" document cited by the applicant in the international application

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

18 August 2020

Date of mailing of the international search report

08 SEP 2020

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer

Lee Young

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/28471

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I: Claims 1-6 drawn to an electrochemical energy storage device.

Group II: Claims 7-15, drawn to a method for synthesizing lithium argyrodites.

--see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-6

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 20/28471

Continuation of Box No. III -- Observations where unity of invention is lacking

The inventions listed in the above-mentioned groups do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group I includes the special technical feature of a solid electrolyte composition, not included in the other groups.

Group II includes the special technical feature of dissolving a mixture of precursors in a solvent, not included in the other group.

Common Technical Features:

The only technical feature shared by Groups I and II that would otherwise unify the groups, is a lithium compound having an argyrodite crystal structure. However, this shared technical feature does not represent a contribution over prior art, because the shared technical feature is disclosed by US 2010/0290969 A1 to Deiseroth et al. (hereinafter Deiseroth).

Deiseroth discloses a lithium compound having an argyrodite crystal structure (para [0006], [0034]: lithium argyrodites of the general formula (I)...Single-phase crystals of the compound Li.sub.6PS.sub.5I were obtained as a white solid).

As the common technical feature was known in the art at the time of the invention, this cannot be considered a special technical feature that would otherwise unify the groups.

Therefore, Groups I-II lack unity under PCT Rule 13.