The present invention provides an energy storage device comprising a cathode region or other element. The device has a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The major active region expands or contracts from a first volume to a second volume during a period of a charge and discharge. The device has a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material configured in a polycrystalline state. The device has an oxygen species configured within the LGPS containing material, the oxygen species having a ratio to the sulfur species of 1:2 and less to form a LGPSO material. The device has a protective material formed overlying exposed regions of the cathode material to substantially maintain the sulfur species within the catholyte material. Also included is a novel dopant configuration of the Li_{x}MnP_{y}S_{z} (LMPS) [M=Si,Ge, and/or Sn] containing material.
Figure 4

- 25°C
- 60°C
- 120°C

Graph showing temperature (°C) on the y-axis and a log scale on the x-axis.
Diagonal lines – active positive electrode material

Speckle – Ionic conductor

Black – Electronic conductor

FIGURE 18A
Horizontal Pin Stripes—Negative electrode current collector
Crosshatch—Solid State Electrolyte
Checkered—Positive electrode current collector

FIGURE 18B
FIGURE 19: Ionic conductivity at 60°C of LGPS, LSPS, LSTPS, and LTPS
FIGURE 20: Arrhenius plot of ionic conductivity. The activation energies are as follows: LGPS – 0.21 eV, LSTPS – 0.25 eV, LSPS – 0.28 eV, LTPS – 0.26 eV
FIGURE 21: Crystal structure from XRD spectra of LSTPS, LSPS, and LTPS
FIGURE 22B: LSTPS $^7$Li NMR
FIGURE 23B: LSTPS $^{31}$P NMR
FIGURE 23C: LSPS $^{31}$P NMR
FIGURE 23D: LGPS $^{31}\text{P}$ NMR
FIGURE 24: Schematic of full cell with solid state catholyte
FIGURE 25: SEM micrograph of cast film of solid state catholyte
SOLID STATE CATHODES AND ELECTROLYTES FOR ENERGY STORAGE DEVICES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a continuation of PCT Application No. PCT/US2014/038238, filed May 15, 2014, entitled SOLID STATE CATHOLYTE OR ELECTROLYTE FOR BATTERY USING Li₂M₅PₓSₙ (M=Si, Ge, and/or Sn), which claims priority to U.S. Provisional Patent Application No. 61/823,047, filed May 13, 2013, and U.S. Provisional Patent Application No. 61/955,096, filed Feb. 5, 2014, the disclosures of which are incorporated herein by reference in their entirety.

BACKGROUND

[0002] In some examples, an embodiment of the present invention relates generally to a solid catholyte or electrolyte material having desired ion conductivity. More particularly, an embodiment of the present invention provides a method and structure for a catholyte material to improve a total ionic conductivity for a cathode to allow for higher mass loading of an active material, faster charge/discharge, and a wider range of operating temperature. Merely by way of example, the invention has been applied to solid state battery cells, although there can be other applications.

[0003] A high level of development has caused an explosion in electronic and communication apparatus. As an example, such apparatus include, among others, a personal computer, a video camera and a portable telephone, commonly termed a “smart phone.” Examples of popular smart phones include the iPhone™ from Apple Inc. of Cupertino, Calif. or those phones using the Android™ operating system of Google Inc. in Mountain View, Calif. Other popular apparatus include electric or hybrid automobiles such as those from Tesla Motors Inc. in Fremont, Calif. or the Prius manufactured by Toyota Motor Corporation. Although highly successful, these popular apparatus are limited by storage capacity and in particular battery capacity. That is, a higher power and higher capacity battery for an electric automobile or a hybrid automobile would be an advance in the automobile industry. A lithium battery has been presently noticed from the viewpoint of a high energy density among various kinds of batteries.

[0004] Liquid electrolyte containing a flammable organic solvent has been used for conventional lithium batteries. Liquid electrolyte can suffer from gassing at high voltage and pose a threat of thermal runaway due to the enthalpy of combustion of the solvents. A lithium battery configured with a solid electrolyte layer (replacing the liquid electrolyte) has been described to improve the safety of the battery. A sulfide solid electrolyte material has been known as a solid electrolyte material used for a solid-state lithium battery. As an example, a solid electrolyte material is described in EP2555307 A1 published Feb. 6, 2013, and filed Mar. 25, 2011, which claims priority to Mar. 26, 2010, in the names of Ryoji Kanno and Masanori Hirayama, assigned to Tokyo Institute of Technology and Toyota Jidoshasha Kabushiki Kai- sha, which is hereby incorporated by reference.

[0005] State of the art solid state batteries are not ready for mass market adoption due to limited power density, mass loading, and manufacturability. Accordingly, techniques for improving a solid-state battery are highly desired.

SUMMARY OF INVENTION

[0006] According to an embodiment of the present invention, techniques related to a solid catholyte or electrolyte material having desired ion conductivity are provided. More particularly, an embodiment of the present invention provides a method and structure for a catholyte material to improve a total ionic conductivity for a cathode to allow for higher mass loading of an active material, faster charge/discharge, and a wider range of operating temperature. Merely by way of example, the invention has been applied to solid state battery cells, although there can be other applications.

[0007] In an example, an embodiment of the present invention provides an energy storage device comprising a cathode region or other element. The device has a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The major active region expands or contracts from a first volume to a second volume during a period of a charge and discharge. The device has a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material configured in a polycrystalline state. The device has an oxygen species configured within the LGPS containing material, the oxygen species having a ratio to the sulfur species of 1:2 and less to form a LGPSO material. The device has a protective material formed overlying exposed regions of the cathode material to substantially maintain the sulfur species within the catholyte material.

[0008] In an alternative example, an embodiment of the present invention provides an energy storage device comprising a cathode region or other element. The device has a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The device has a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state or variations or combinations thereof. The device has an oxygen species configured within the LGPS or LSPS containing material. The oxygen species has a ratio to the sulfur species of 1:2 and less to form a LGPSO or LSPSO material. The device has a confinement material formed overlying exposed regions of the cathode active material to minimize reaction between the LGPS or LSPS containing material and the active material.

[0009] In an alternative example, an embodiment of the present invention provides an energy storage device comprising a cathode region or other element. The device includes a major active region comprising a plurality of first active regions spatially disposed within the cathode region, and a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, each of the plurality of active regions has a median
diameter ranging from about 20 nm to about 3 μm. In another example, each of the plurality of active regions has a median diameter ranging from about 20 nm to about 8 μm.

[0010] In an example, the cathode material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state. In an example, the device has a plurality of particles characterizing the cathode material. In an example, each of the plurality of particles is interconnected to another via a necking arrangement. Each particle has a dimension characterized by a particle diameter to neck ratio dimension ranging from 1% to greater than 100%. In some examples, the plurality of particles is arranged to form a polycrystalline structure having a porosity of less than 30% of a total volume of the cathode region. In an example, each of the plurality of particles in the cathode material is substantially homogeneous in a micro-scale while configured in the polycrystalline structure in a ten to one hundred micron scale. In an example, the cathode region comprises an active material, the active material comprising iron and fluorine. In an example, the cathode material is selected from one of Li₄Si₅P₄S₁₀ or Li₄GeP₄S₁₀. In an example, the cathode material is provided by annealing Li₄S, P₅S₁₀, and GeS₄ or SiS₄ at 550 °C. for greater than about 4 hrs in stainless steel reactors sealed from the air, or other variations. In an example, the cathode material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogeneous thickness of material defining the cathode region. In an example, the cathode material comprising a plurality of clusters, each of which has a median diameter ranging from about 10 nm to about 300 nm. In an example, the cathode material comprising a plurality of shell structures around the cathode active regions. In an example, the cathode material configured as a plurality of particles, each of the particles having a median diameter ranging from about 20 nm to about 300 nm. In an example, the cathode material is substantially free from oxygen species.

[0011] In an example, the oxygen species ranges from less than 1 percent to 20 percent of the LGPS or LSPSO containing material. In an example, the sulfur containing species ranges from about 25 to 60 percent of the LGPS or LSPSO material. In an example, the device has an oxygen species configured within the LGPS or LSPSO containing material. In an example, the oxygen species has a ratio to the sulfur species of 1:2 and less to form a LGPSO or LSPSOO material.

[0012] The device has a confinement material formed overlying exposed regions of the cathode active material to minimize reaction between the LGPS or LSPS containing material and the active material. In an example, the confinement material is configured as a barrier material and/or the confinement material substantially preventing an interaction of the sulfur containing species with an element within the major active region. In an example, the confinement material is configured to selectively allow a lithium species to traverse through the confinement material. In an example, the major active region is greater than 50 percent by volume of the cathode region. The active region is desirably as great a fraction as possible of the cathode, possibly up to 70% or even 80%. In an example, the device has a second confinement material overlying each of the plurality of active regions.

[0013] In an example, the device has a polymer material configured within a vicinity of the catholyte material, the polymer material serving as a binder material. In an example, the polymer material is formed overlying the catholyte material. In an example, the polymer material serves as an electrolyte. In an example, the polymer material has an ionic conductivity serves as an electrolyte. In an example, the polymer material is configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction.

[0014] In an example, an embodiment of the present invention provides an energy storage device comprising a catholyte material spatially confined within a spatial region of the energy storage device. The material includes a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline, nanoporous or amorphous state. The device has a room temperature ionic conductivity ranging from 10⁻⁴ to 5×10⁻⁴ S/cm characterizing the LGPS or LSPS material and an electrical conductivity less than 10⁻⁴ S/cm characterizing the LGPS or LSPS material.

[0015] In an example, an embodiment of the present invention provides an energy storage device comprising a catholyte material spatially confined within a spatial region of the energy storage device. The material has a lithium, silicon, phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state. The device has a room temperature ionic conductivity ranging from 10⁻⁴ S/cm to 5×10⁻⁴ S/cm characterizing the LSPS material, an electrical conductivity less than 10⁻⁴ S/cm characterizing the LSPS material, and an XRD 20 scan characterized by a primary peak at 33°±1°, 31°±1°, or 43°±1°.

[0016] In an example, an embodiment of the present invention provides an energy storage device comprising a cathode region or other region(s). The device has a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The major active region expands or contracts from a first volume to a second volume during a period of a charge and discharge. The device has a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material configured in a polycrystalline state. The catholyte material is characterized by an XRD as measured in counts per second characterized by a first major peak between about 41 to 45° 2theta (i.e., 2θ) and a second major peak between about 30 to 35° 2theta and a third major peak between 51-54° 2-theta; wherein the first major peak is higher in intensity than either the second major peak or the third major peak.

[0017] In an example, an embodiment of the present invention provides a method for manufacturing an energy storage device. The method includes forming a cathode region, the cathode region comprising a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The major active region expands or contracts from a first volume to a second volume during a period of a charge and discharge; a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions
not occupied by the first active regions, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material configured in a polycrystalline state.

In an example, an embodiment of the present invention provides a solid catholyte material or other material. The material includes at least a lithium element, a silicon element, a phosphorous element, a sulfur element, and an oxygen element. In an example, the catholyte is characterized by a major XRD peak at a peak position of 20=30±1° in an X-ray diffraction measurement using a CuKα line, or a peak of 20=33±1° or a peak of 20=43±1°.

In an alternative example, the invention provides a solid catholyte material containing Li₅Si₃PS₅S₃O₉, where 2≤α≤8, 0.5≤β≤2.5, 4≤α≤12, d=3, wherein any impurities are less than 10 atomic percent. In an example, the solid ion conducting material comprising Li, Si, P, and S is characterized by primary Raman peaks at 418±10 cm⁻¹, 385±10 cm⁻¹, 286±10 cm⁻¹, and 1614±10 cm⁻¹ when measured at room temperature with a Renishaw inVia Raman microscope system with a laser wavelength of 514 nm.

In some examples, an embodiment of the present invention achieves these benefits and others in the context of known process technology. However, a further understanding of the nature and advantages of an embodiment of the present invention may be realized by reference to the latter portions of the specification and attached drawings.

According to an embodiment of the present invention, techniques related to a solid catholyte material having desired ion conductivity are provided. In particular, an embodiment of the present invention provides a method and structure for a catholyte material to improve total ionic conductivity for a cathode to allow for higher mass loading of an active material, faster charge/discharge, and a wider range of operating temperature. More particularly, an embodiment of the present invention provides a novel dopant configuration of the Li₅MP₅S₅O₉ (LMPS) [M=S, Si, Ge, and, or, Sn] containing material. Merely by way of example, the invention has been applied to solid state battery cells, although there can be other applications. In some examples, M is selected from Si, Ge, Sn, or combinations thereof. In some other examples, M is selected from Si, Sn, or combinations thereof.

In an example, an embodiment of the present invention provides for a solid state battery with improved total ionic conductivity for a cathode, higher mass loading of active material (therefore higher energy density), faster charge/discharge, and a wider range of operating temperature for the solid state architecture eliminates the need for a flammable liquid electrolyte and therefore provides a safer alternative.

In an example, an embodiment of the present invention provides a dopant species configured within the LMPS containing material. In an example, the dopant species is characterized by increasing an ionic conductivity of the LMPS material from a first ionic conductivity value to a second ionic conductivity value. Such dopant species may be provided in any one of the examples described below. In an example, an embodiment of the present invention provides an energy storage device comprising a cathode region or other element. The device has a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The major active region expands or contracts from a first volume to a second volume during a period of a charge and discharge. The device has a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material configured in a polycrystalline state. The device has an oxygen species configured within the LGPS containing material, the oxygen species having a ratio to the sulfur species of 1:2 and less to form a LGPSO material. The device has a protective material forming overlying exposed regions of the cathode material to substantially maintain the sulfur species within the catholyte material.

In an alternative example, an embodiment of the present invention provides an energy storage device comprising a cathode region or other element. The device has a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The device has a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon, phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state or variations. The material may have an oxygen species configured within the LGPS or LSPS containing material. The oxygen species has a ratio to the sulfur species of 1:2 and less to form a LGPSO or LSPSO material. The device has a confinement material forming overlying exposed regions of the cathode active material to minimize reaction between the LGPS or LSPS containing material and the active material.

In an alternative example, an embodiment of the present invention provides a dopant species for a cathode of an energy storage device comprising a cathode region or other element. The device includes a major active region comprising a plurality of first active regions spatially disposed within the cathode region, and a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an example, each of the plurality of active regions has a size ranging from about 20 nm to about 3 µm.

In an example, the catholyte material comprises a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material, or a lithium, silicon, phosphorous, and sulfur ("LSPS") containing material, or a lithium, tin, phosphorous, and sulfur ("LTPS") containing material. Each of the compounds may be configured in a polycrystalline or amorphous state. In an example, the device has a plurality of particles characterizing the catholyte material. In an example, each of the plurality of particles is interconnected to another via a necking arrangement. Each particle has a dimension characterized by a neck to particle diameter ratio dimension ranging from 1% to greater than 90% to form a polycrystalline structure having a porosity of less than 30% of a total volume of the cathode region. In an example, each of the plurality of particles in the catholyte material is substantially homogeneous, or can have variations. For example, the particles can have a diameter ranging from about 20 nm to about 1 micron. In an example, the cathode region comprises an active material, the active material
comprising iron and fluorine. In an example, the cathode region comprises an active material, the active material comprising one or more of LiFePO₄, LiCoO₂, LiMn₂O₄, LiNi₁/₃Mn₁/₃O₂, Li(NiCoAl)O₂, or other conventional lithium battery cathode materials. In an example, the cathode material is selected from one of Li₃SiP₂S₅ or Li₃GeP₂S₅. In an example, the cathode material is provided by annealing Li₂S, P₂S₅, and GeS₂ or SiS₂ at 550 °C. for greater than about 4 hrs in stainless steel reactors sealed from the air, or other variations. In an example, the cathode material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogeneous thickness of material defining the cathode region. In an example, the cathode material comprising a plurality of clusters, each of which has a diameter ranging from about 10 nm to about 300 nm. In an example, the cathode material comprising a plurality of shell structures around the cathode active regions. In an example, the cathode material configured as a plurality of particles, each of the particles having a diameter ranging from about 20 nm to about 300 nm. In an example, the cathode material is substantially free from oxygen species.

In an example, the oxygen species range from less than 1 percent to 20 percent of the LGPSO or LSPSO material. In an example, the sulfur containing species range from about 25 to 60 percent of the LGPSO or LSPSO material. In an example, the device has an oxygen species configured within the LGPS or LSPS containing material. In an example, the oxygen species has a ratio to the sulfur species of 1:2 and less to form a LGPSO or LSPSO material.

In an example, the LMPs material is doped with a combination of metal species on the M site. The composition range includes Li₃(Si₃Sn)P₅S₁₀ (“LSTPS”), Li₃(SiGe)P₂S₇, Li₃(SiSn)P₅S₁₀, and Li₃(SiGeSn)P₅S₁₀, including variations in a ratio of Si to Sn and other alternatives. The material may have an oxygen species configured within the LSTPS, LGPS, LGPTS, or LSGTPS containing material to form LSTPSO, LGPSO, LGPTSO, or LSGTPOS. The oxygen species has a ratio to the sulfur species of 1:2 and less.

In an example, the device has a confinement material formed overlying exposed regions of the cathode active material to minimize reaction between the LGPS or LSPS containing material and the active material. In an example, the confinement material is configured as a barrier material and/or the confinement material substantially preventing an interaction of the sulfur containing species with an element within the major active region. In an example, the confinement material is configured to selectively allow a lithium species to traverse through the confinement material. In an example, the major active region is greater than 50 percent by volume of the cathode region. The active region is desirably as great a fraction as possible of the cathode, possibly up to 70% or even 80%. In an example, the device has a second confinement material overlying each of the plurality of active regions.

In an example, an embodiment of the present invention achieves these benefits and others in the context of known process technology. However, a further understanding of the nature and advantages of an embodiment of the present invention may be realized by reference to the latter portions of the specification and attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a simplified diagram illustrating mixing cathode active material with catholyte to improve overall ion conductivity according to an example of an embodiment of the present invention.

Fig. 2 is a simplified diagram illustrating mixing smaller particles of catholyte with active cathode material for enhancing ionic and electronic conductivity according to an example of the present invention.

Fig. 3A and 3B are a simplified diagram illustrating a cross-section of a battery device according to an example of the present invention.

Fig. 4 is a simplified diagram illustrating LSPS ionic and electronic conductivity Arrhenius plot according to an example of the present invention.

Fig. 5 shows SEM of LSPS, LGPS, illustrating a necking behavior and forming connecting networks according to an example of the present invention.

Fig. 6 shows LSPS XRD scan in air and peak location derived from material that is crystalline from the annealing process according to an example of the present invention.

Fig. 7 shows an XRD pattern & peak positions of LSPS taken in an argon environment according to an example of the present invention.

Fig. 8 shows an LSPS XPS scan and stoichiometry including LSPS specific peak shifts according to an example of the present invention.

Fig. 9 shows XRD patterns and peaks of several LGPS powders taken in an argon atmosphere according to an example of the present invention.

Fig. 10 shows a cyclic voltammogram of LGPS using a lithium reference/couter electrode and stainless steel working electrode according to an example of the present invention.

Fig. 11 shows an illustration of Raman spectroscopy signature of several LGPS samples according to an example of the present invention.

Fig. 12 shows an illustration of Raman spectroscopy of LGPS, comparing to precursors according to an example of the present invention.

Fig. 13 shows an illustration of an LGPS ionic conductivity Arrhenius plot according to an example of the present invention.

Fig. 14 shows LGPS ionic conductivity as a function of P and Ge concentrations according to an example of the present invention.

Fig. 15 shows composition of P and Ge in pressed pellets of Li₃GeP₂S₅ measured by X-ray photoelectron spectroscopy (XPS) as a function of Li₃SiP₂S₅:GeS₂ precursor ratio.

Fig. 16 shows ion conductivity plotted as a function of temperature for samples according to an embodiment of the present invention.

Fig. 17 shows an XRD spectrum of an LSPS sample with conductivity of 9e⁻4 S/cm at 30 °C.

Fig. 18A is a simplified illustration of an electrode material (including an active positive electrode material, ionic conductor, and electronic conductor) according to an example of the present invention.

Fig. 18B is a simplified illustration of a negative electrode current collector, a solid state electrolyte, and a positive electrode current collector according to an example of the present invention.
FIG. 19 illustrates ionic conductivity at 60°C of LGPS, LSPS, LSTPS, and LTPS according to examples of the present invention.

FIG. 20 illustrates an Arrhenius plot of ionic conductivity for activation energies are as follows: LGPS—0.21 eV, LSTPS—0.25 eV, LSPS—0.28 eV, LTPS—0.26 eV, in various examples according to the present invention.

FIG. 21 illustrates a crystal structure from XRD spectra of LSTPS, LSPS, and LTPS according to examples of the present invention.

FIGS. 22A, 22B, 22C, and 22D are examples of 3Li NMR plots.

FIGS. 23A, 23B, 23C, and 23D are examples of 3P NMR plots.

FIG. 24 illustrates a schematic of full cell with solid state cathode in an example according to the present invention.

FIG. 25 is a SEM micrograph of cast film of solid state cathode according to an example of the present invention.

DETAILED DESCRIPTION OF THE SPECIFIC EMBODIMENTS

According to an embodiment of the present invention, techniques related to a solid cathode or electrolyte material having desired ion conductivity are provided. More particularly, an embodiment of the present invention provides a method and structure for a cathode material to improve a total ionic conductivity for a cathode to allow for higher mass loading of an active material, faster charge/discharge, and a wider range of operating temperature. Merely by way of example, the invention has been applied to solid state battery cells, although there can be other applications.

As background, poor ionic conductivity of the cathode in a battery imposes strong limitations to overall performance. By optimizing the low ionic conductivity cathode active material with a high ionic conductivity ceramic cathode, it is possible to improve the overall cathode conductivity. In this description, the ceramic cathode is either LGPS or LSPS, which possesses Li ion conductivity greater than 1×10⁻⁶ S/cm at 60°C. An overall ion conductivity of the cathode (1×10⁻⁶ S/cm) can be achieved by adjusting the volume ratio of the active cathode material (ranging from about 30% to about 85%) to the cathode. To improve electronic conductivity to match the ionic conductivity, carbon can be added as a third component or pre-coated onto the cathode active material.

As in one example, the composition of the cathode is Li₂₅Ge₈S₃₀, where X=Ge for LGPS or Si for LSPS. LGPS and LSPS are synthesized using similar starting materials: Li₃S₄, P₂S₉, and GeS₂ or SiS₂. The synthetic approach includes ball milling of the precursors to create a homogeneous mixture, followed by annealing at 550°C in an argon-tight vessel, and additional ball milling of the resultant product to achieve the desired particle size. Alternatively, the material can be made by evaporating the pre-annealed powder or co-evaporating Li₂S, P₂S₉, and SiS₂/GeS₂ powders. As a thin film, the compounds could also be used as electrolytes.

LSPS as described herein can be used as a thin film electrolyte. Means to deposit LSPS as a thin film are known to those skilled in the art. As an example, PVD methods such as PLD, sputtering, thermal, e-beam, and/or flash evaporation can be used. As a specific, non-limiting example of one deposition by thermal evaporation, the process is as follows: 1. Clean a smooth stainless steel substrate (430 alloy) with a kitchen sponge and simple green. Rinse in water. Rinse in acetone. Rinse in water. Microwave for two minutes submerged in water. 2. Load substrate into evaporator. 3. Prepare LSPS material as described above and press LSPS in the ratio of 5:1 S₃P₅S₆:SiS₂ into pellets. Load pellets into evaporator crucible. Total mass of LSPS is 1.5 g. 4. Pump evaporator down to base pressure of ~1e-5 torr. 5. Evaporate for 25 minutes with heater at ~1400 degrees C. while rotating substrate. 6. Purge evaporator twice with inert gas. 7. Evaporate inert metal, e.g. Pt or Au, as top contact.

In an example, a benefit of replacing Ge with Si is to address the high cost of Ge, among other things. The cost of Ge is approximately 800 times of Si. The overall material cost of the catholyte drops by a factor of 10 if Ge is replaced with Si. Use of Si in place of Ge also appears to improve the stability of the material interface to Li. Further details of an embodiment of the present invention can be found throughout the present specification and more particularly below.

As used herein, the phrase “substantially free from oxygen species,” refers to a material having less than 5% oxygen.

As used herein, the phrase “substantially prevent,” refers to material wherein the catholyte or cathode active material do not react to form a separate phase that prevents a long cycle life, wherein a long cycle life is characterized by greater than 100 cycles. If the catholyte or cathode active material substantially react, e.g., more than 1% mass fraction of the active material reacts, to form a separate phase that is not useful for battery performance, the cycle life of the cathode or of the battery is shortened. As such, the battery cycle life is maintained at a long cycle life (>100 cycles) when the catholyte or cathode active material do not substantially react to form a detrimental separate phase.

As used herein, the phrase “substantially homogeneous thickness,” refers to a material having a roughness of less than 1 micron.

As used herein, the phrase “substantially free from oxygen” refers to a material having less than 5% oxygen.

As used herein, the phrase “selectively allow a lithium species to traverse” through the material,” refers to material that allows lithium species to diffuse therethrough by at least 7 or 8 orders of magnitude more than another diffusion species. As used herein, “selectively allow” also refers to >C/A rate capability for charge/discharge with lithium while providing for long (>100 cycles) cycle life.

Active material mass loading in a cathode determines the energy density of a battery. Increasing the accessible active material mass loading per surface area increases the overall system energy density by increasing the ratio of active material to inactive components including current collectors and separators. The active material mass loading is limited by the total ionic and electronic conductivity through the cathode. By including a high Li⁺ ionic conductivity catholyte in the cathode, lithium reversibly shuttles throughout the entire cathode thickness and reduces voltage losses to overpotential. The use of ceramic material also may reduce/eliminate the formation of a solid electrolyte interface (SEI) and provide a wider voltage stability window.

FIG. 1 is a simplified diagram illustrating mixing cathode active material with catholyte (MEIC) to improve overall ion conductivity according to an example of the
present invention. As shown, mixing occurs with active material, which can be any suitable active material with catholyte material, which can be Li$_{x}$XP$_{y}$S$_{z}$, where X=Ge (for LGPS) or Si (for LSPS), and combinations thereof, or the like. As shown, the catholyte material is coated or configured around or within a vicinity of the active material. As shown is a core shell structure, although there can be variations. The core-shell structure may be fabricated by solid-state synthesis such as co-milling or mechanoactivation, liquid phase synthesis such as precipitation or heterogeneous reaction, or vapor phase synthesis such as CVD or evaporation. In an example, the present catholyte material has a high ion conductivity of 10$^{-2}$ S/cm and greater.

[0069] FIG. 2 is a simplified diagram illustrating mixing smaller particles of MEIC with active cathode material in the ideal geometry for enhancing ionic and electronic conductivity according to an example of the present invention. As shown, smaller particles of MEIC are mixed with active cathode material to form a plurality of clusters representing intermixed active cathode material spatially disposed with the MEIC particles. In another example, the illustration shows engineered sized catholyte particles to improve and or to optimize ion conductivity to form a percolating network structure.

[0070] FIG. 3 is a simplified diagram illustrating a cross-section of a battery device according to an example of the present invention. As shown, the battery device comprises an anode region, a first current collector, an electrolyte, a second current collector, and a cathode region. Further details of battery device can be found throughout the present specification and more particularly below, and also in reference to FIG. 3A.

[0071] In an example, the anode region comprises a major active region comprising lithium. The anode region has a thickness ranging from about 0.1 μm to about 100 μm, but can include variations. In an embodiment, the anode region is created in situ by plating lithium from the cathode during the first charging cycle, among other techniques.

[0072] Each of the current collectors is a metal foil or a metal coating. Each current collector has a major surface region and preferably has a thickness ranging from 100 nm to 25 μm, although there may be variations. In an example, the negative current collector is a foil made of copper, nickel, nickel-coated copper, iron-coated copper, copper-coated aluminum, titanium, stainless steel, and coatings of these and other materials known not to alloy with lithium, and configured to the anode region. In another example, the positive current collector is aluminum foil or carbon-coated aluminum foil, though other materials stable at >3.5V vs Li (either intrinsically or via a self-passivating mechanism) can be used. The positive current collector is configured to the cathode region. In the case that one or both current collectors is a metal coating rather than a foil, it may be created with standard routes such as electropolishing, electroless plating, PVD, metal nanoparticle sintering, and/or sol-gel with post-reduction. In this example, configured includes adhering or bonding the current collector to that which it is configured.

[0073] As shown, the battery device has an electrolyte. The electrolyte is, in some examples, a fast lithium ion conductor with a conductivity of greater than 10$^{-5}$ S/cm. Examples of such materials include garnet, LiPON, antiperovskite, LISICON, thio-LISICON, sulfide, oxysulfide, polymer, composite polymer, ionic liquid, gel, or organic liquid. The electrolyte has a thickness ranging from about 0.1 μm to about 40 μm, but includes variations. In some examples, the electrolyte thickness is 25 μm, i.e., 25 microns. In some examples, the electrolyte thickness is 25 μm or less, i.e., 25 microns or less.

[0074] In an example, the cathode region comprises a major active region comprising a plurality of first active regions spatially disposed within the cathode region. The cathode region includes a catholyte material spatially confined within a spatial region of the cathode region. In an example, the material is spatially disposed within spatial regions not occupied by the active regions, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon, phosphorous, and sulfur ("LSPS") containing material, each of which is configured in the amorphous state. The catholyte material has an ion conductivity greater than 10$^{-4}$ S/cm and preferably greater than 10$^{-3}$ S/cm. The catholyte material is configured to form a percolating network through the cathode. The catholyte material is therefore made with a particle size that is smaller than the active region particle size. For example, the median catholyte particle can be less than a micrometer three times or more smaller than the median active particle size. The particle size may be measured by techniques familiar to those skilled in the art such as a Horiba particle size analyzer. The catholyte material may alternately be configured in a core-shell structure as a coating around the cathode active material. In a further variation, the catholyte material may be configured as nanorods or nanowires. The cathode is then densified, for example in a calender press, to reduce porosity, thereby increasing the density of the cathode.

[0075] The cathode region also includes electronically conducting species such as carbon, activated carbon, carbon black, carbon fibers, carbon nanotubes, graphite, graphene, fullerene, metal nanowires, super P, and other materials known in the art. The cathode region further comprises a binder material to improve the adhesion of the cathode to the substrate and the cohesion of the cathode to itself during cycling.

[0076] In an example, the catholyte material has an oxygen species configured within the LGPS or LSPS containing material. In an example, the oxygen species has a ratio to the sulfur species of 1:2 and less to form a LGPSO material or LSPSO material. In an example, the oxygen species is less than 20 percent of the LGPSO material. Of course, there can be variations which are embraced by other embodiments of the invention.

[0077] In an example, the catholyte material has a protective material overlying exposed regions of the cathode active material to minimize a reaction between the catholyte containing material and the active material. In an example, the protective material is configured as a barrier material. The barrier material may be AlF$_3$, LiF, Li$_2$AI$_2$F$_7$, LiPO$_4$, Al$_2$O$_3$, TiO$_2$, lithium titanate, lithium beta alumina, LiNbO$_3$, LiCoO$_2$, FeOF, FeO$_2$, or other materials stable in the cathode potential range. The barrier material substantially prevents a reaction between the active material and the catholyte material. The confinement material substantially prevents an interaction of the sulfur containing species with an element within the major active region. The major active region is preferably about 50 percent or more of the cathode region; and the catholyte material is preferably about 30 percent or less of the cathode region. In an example, the protective material is configured to selectively allow a lithium species
to traverse through the protective material. As an example, the protective material may comprise a plurality of spatial openings to allow the lithium species to traverse through the protective material. Each of the openings has a size ranging from about 1 nm² to about 100 nm². As another example, the protective material may comprise a lithium conductive material.

[0078] Optionally, the device has a second protective material overlying each of the plurality of active regions. The second protective material is similar in characteristic as the first confinement material. In a variation, the protective material may be configured around the active material or around the ion conductive material. Alternatively, the device can include multiple confinement materials, among other variations.

[0079] In an example, the catholyte comprises LiX, S2O3, or Si, 2≤a≤6, 0.5≤b≤2.5, 4≤c≤10, and m≥3 or other variations. Further details of the LSPS material characterization can be found throughout the present specification and more particularly below. See, for example, the XPS, XRD, Raman, set forth herein.

[0080] In another example, the LSPS or LGPS material is characterized by Li1-xSxP2S8 or Li1-xGeP2S8, where 2≤a≤8, 0.5≤b≤2.5, 4≤c≤12, d≥3.4

[0081] In yet another example, the LSPS or LGPS material is characterized by a catholyte selected from either Li1-xSxP2S8 or Li1-xGeP2S8 wherein 2≤a≤10, 0.5≤b≤2.5, 4≤c≤12, d≥3.

[0082] In an example, the catholyte material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogeneous thickness of material defining the cathode region. In an example, the catholyte material comprises a plurality of clusters, each of which is separable. Alternatively, the catholyte material comprises a plurality of shell structures around the active material particles. In other embodiments, the catholyte material is configured as a plurality of particles.

[0083] In an example, the catholyte material is characterized as a solid. That is, the material has a substantially fixed compound structure, which behaves like a solid rather than a fluid. In an example, the solid catholyte material is fabricated by physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD), and solid state reaction of powders, mechanical milling of powders, solution synthesis, evaporation, or any combination thereof. In an example, the catholyte material is mixed with the active material in a mixer or mill or with different configurations of physical vapor deposition, optionally mixed with carbon, and coated onto a substrate by gravure, comma coating, meyer rod coating, doctor blading, slot die coating, or with a conventional technique. In an example, the catholyte material is coated directly on the active material with a vapor phase growth, mechanofusion, liquid phase growth, deposition on particles in a fluidized bed or rotary reactor, or combinations thereof, or the like. Of course, there are various alternatives, modifications, and variations.

[0084] In an alternative example, the device further comprises a polymer material configured within a vicinity of the catholyte material, the polymer material comprising a lithium species. The polymer material is formed overlying the catholyte material, the polymer material comprising a lithium material. The polymer material configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction. An example of the polymer material includes polyacrylonitrile, poly-ethylene oxide, PdCl2, PdH2-PEP, rubbers like butadiene rubber and styrene butadiene rubber, among others.

[0085] In an example, the silicon material has a purity of 98 to 99.9999%, the lithium has a purity of 98 to 99.9999%, phosphorous has a purity of 98 to 99.9999%, and the sulfur has a purity of about 98 to 99.9999%, although there can be variations.

[0086] FIG. 4 is a simplified diagram illustrating LSPS ionic conductivity Arrhenius plot according to an example of the present invention. As shown, conductivity is plotted against 1/T. Conductivity is plotted in an Arrhenius plot. As an example, a conventional solid catholyte material is below 10⁻⁴ S/cm for ionic conductivity, which is well below the present materials and techniques. Arrhenius plot of the ionic conductivity of Li1-xSxP2S8 and Li1-xSxP2S8 pressed pellets measured by electrochemical impedance spectroscopy with indium blocking electrodes. Pellets were made by mixing 5:1 ratios of Li1-xSxP2S8:GeS6 for Li1-xSxP2S8 and Li1-xSxP2S8:SiS6 for Li1-xSxP2S8 by high energy milling in a zirconia jar with zirconia media, followed by annealing at 550°C. For 8 hrs in stainless steel VCR Swagelok reactors. Pellets were made from the powders by pressing at 5 MPa. LSPS materials may also be synthesized by annealing in a quartz or silica reactor. LPS may be synthesized from starting precursors that include the elemental compounds (Li and/or Si and/or P and/or Sn and/or Ge and/or S) alone or in combination with the compounds (Li1-xSxP2S8:SiS6:SnS2, P2S8, GeS6).

[0087] FIG. 5 shows LSPS and LGPS, SEM including a necking behavior indicating a good chance of forming connecting networks according to an example of the present invention. As shown, LSPS has features at a ten-nanometer scale, LGPS has features at a 100-nanometer scale. As shown, the material is configured with a plurality of particles each of which is interconnected to each other via a necking arrangement, rather than a single point or a “billiard ball” contact, which would limit conductivity between particles. In an example, the particle-to-neck ratio dimension can be 1% to greater than 100% to form a polycrystalline structure having a porosity of less than 30% of the total volume of the material. In an example, the material is substantially homogeneous in a micro-scale while configured in the polycrystalline structure in a ten to one hundred micron scale. In an example, the material with a material active, such as LiCoO2 for example, or other variations. As shown illustrate morphology of Li1-xSxP2S8 and Li1-xGeP2S8 pressed pellets. Grain sizes of these synthesized materials are 1-10 μm (synthesized by annealing Li1-xSxP2S8, GeS6 or SiS6, at 550°C. For 8 hrs in stainless steel VCR Swagelok reactors). Of course, there can be variations.

[0088] FIG. 6 shows LSPS XRD scan in air derived from material that is crystalline from the annealing process according to an example of the present invention. As shown is the peak position, intensity, and FWHM data below. As shown is XRD 2θ scan of Li1-xSxP2S8:SiS6:SnS2. The Li14xS1-xP14xS14xO14 powder is synthesized by high energy milling 5:1:1 mixture of Li1-xSxP2S8, and SiS6 in a ZnO2 jar with ZnO2 media, followed by annealing at 550°C. For 8 hrs in stainless steel VCR Swagelok reactors. Pellets were made from the powders by pressing at 5 MPa.
<table>
<thead>
<tr>
<th>2-theta(°)</th>
<th>d(Å)</th>
<th>Normalized intensity</th>
<th>FWHM(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.1722</td>
<td>3.40207</td>
<td>0.16</td>
<td>0.5674</td>
</tr>
<tr>
<td>27.184</td>
<td>3.27771</td>
<td>0.45</td>
<td>0.2801</td>
</tr>
<tr>
<td>27.0566</td>
<td>3.18885</td>
<td>0.41</td>
<td>0.2701</td>
</tr>
<tr>
<td>30.0299</td>
<td>2.88874</td>
<td>0.12</td>
<td>1.5391</td>
</tr>
<tr>
<td>33.3519</td>
<td>2.6843</td>
<td>1.00</td>
<td>0.2044</td>
</tr>
<tr>
<td>33.8262</td>
<td>2.64773</td>
<td>0.34</td>
<td>2.0815</td>
</tr>
<tr>
<td>41.3252</td>
<td>2.18094</td>
<td>0.12</td>
<td>0.3451</td>
</tr>
<tr>
<td>52.1143</td>
<td>1.75356</td>
<td>0.21</td>
<td>0.2782</td>
</tr>
<tr>
<td>52.9009</td>
<td>1.72632</td>
<td>0.38</td>
<td>0.2964</td>
</tr>
<tr>
<td>54.6355</td>
<td>1.67845</td>
<td>0.04</td>
<td>0.8444</td>
</tr>
<tr>
<td>56.4607</td>
<td>1.62844</td>
<td>0.05</td>
<td>0.5958</td>
</tr>
</tbody>
</table>

**[0089]** FIG. 7 shows an XRD pattern and peak positions of LSPS taken in an argon environment according to an example of the present invention. As shown are angle and height data from the XRD pattern. As shown, the LSPS material is configured having a XRD pattern having a major peak along a 2-theta direction and height provided in the table below and FIG. 7 showing an X-ray diffraction of a Li$_x$SiP$_2$S$_6$O$_{14}$ pressed pellet. The Li$_x$SiP$_2$S$_6$O$_{14}$ powder is synthesized by high energy ball milling 5:1 mixtures of Li$_2$S, P$_2$S$_5$, and SiS$_2$ in a ZrO$_2$ jar with ZrO$_2$ media, followed by annealing at 550°C. For 8 hrs in stainless steel VCR Swagelok reactors. Pellets were made from the powders by pressing at 5 MPa.

<table>
<thead>
<tr>
<th>2-theta(°)</th>
<th>Normalized intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.4</td>
<td>0.29</td>
</tr>
<tr>
<td>19.1</td>
<td>0.29</td>
</tr>
<tr>
<td>20.3</td>
<td>0.32</td>
</tr>
<tr>
<td>27.1</td>
<td>0.39</td>
</tr>
<tr>
<td>27.9</td>
<td>0.39</td>
</tr>
<tr>
<td>30.1</td>
<td>0.42</td>
</tr>
<tr>
<td>30.9</td>
<td>0.55</td>
</tr>
<tr>
<td>33.4</td>
<td>0.43</td>
</tr>
<tr>
<td>43.8</td>
<td>1.00</td>
</tr>
<tr>
<td>50.4</td>
<td>0.41</td>
</tr>
<tr>
<td>53.1</td>
<td>0.44</td>
</tr>
</tbody>
</table>

**[0090]** FIG. 8 shows an LSPS XPS scan and stoichiometry including LSPS specific peak shifts according to an example of the present invention. As shown are peaks associated with lithium, silicon, phosphorus, sulfur, and oxygen to characterize the material. Peak locations are at approximately 58 eV, 104 eV, 134 eV, 164 eV, and 533 eV respectively when calibrated versus a carbon peak at 284 eV. As shown is XPS of Li$_x$SiP$_2$S$_6$O$_{14}$ 4Li$_x$ SiP$_2$S$_6$O$_{14}$ pressed pellet. The Li$_x$SiP$_2$S$_6$O$_{14}$ powder is synthesized by high energy ball milling 5:1 mixture of Li$_2$S, P$_2$S$_5$, and SiS$_2$ in a ZrO$_2$ jar with ZrO$_2$ media, followed by annealing at 550°C. For 8 hrs in stainless steel VCR Swagelok reactors. Pellets were made from the powders by pressing at 15 MPa.

**[0091]** FIG. 9 shows XRD patterns and peaks of several Li$_2$GeP$_2$S$_6$ powders taken in an argon atmosphere according to an example of the present invention. As shown, ratios refer to the proportion of Li$_2$S to P$_2$S$_5$ to GeS$_2$ initially mixed to form the final compound. Actual compositions are Li$_2$GeP$_2$S$_6$O$_{14,5}$ and Li$_2$GeP$_2$S$_6$O$_{12,5}$. Of course, there can be variations. As shown are four different compositions in the Figure. Compensations in the ratios 5:1:1, 45:2:1, 15:2:1 are show below.

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Normalized Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>202</td>
<td>0.22</td>
</tr>
<tr>
<td>286</td>
<td>0.22</td>
</tr>
<tr>
<td>383</td>
<td>0.53</td>
</tr>
</tbody>
</table>

**[0092]** FIG. 10 is a plot of cyclic voltammogram of LGPS using a lithium reference/couter electrode and stainless steel working electrode. Li plating and stripping is observed at 0 V vs. Li/Li, and the lack of features up to 5 V indicates excellent electrochemical stability. The measurement is provided to indicate electrochemical stability, as indicated by the substantially straight line without peaks or imperfections. The straight line originates in an ion conductor from a plating current to form both positive and negative current as the voltage varies from negative to positive. As shown, no significant current is observed in the positive voltage region on the voltage curve, which indicates electrochemical stability: (a) Cyclic voltammogram of Li$_x$GeP$_2$S$_6$O$_{14}$ pressed pellet using a lithium reference/couter electrode and stainless steel working electrode. (b) Cyclic voltammogram of Li$_x$GeP$_2$S$_6$O$_{14}$ pressed pellet using a lithium reference/couter electrode and Nickel foil working electrode. In both cases, clear Li plating and stripping occurs at 0 V vs. Li/Li$^+$. 

**[0093]** FIG. 11 is an illustration of Raman spectroscopy signatures of several LGPS samples. As shown, the Raman signature indicates LGPS material configuration. As shown is Raman spectroscopy of various Li$_2$GeP$_2$S$_6$ pressed pellets.
The Table shows Raman peaks from LGPS 15:2:1 (the ratios refer to the relative amounts of $Li_3S_2P_2S_6Ge_2S_2$ precursors used in the synthesis). Note that Raman peaks shift slightly with the laser wavelength. Of course, there can be other techniques to characterize the subject material. However, the Raman signature for these pellets is similar from sample to sample.

**FIG. 12** illustrates a Raman spectroscopy of LGPS, compared to its precursors. New features in Raman spectra can be clearly observed in LGPS versus the precursors. As shown is Raman spectroscopy of $GeS_2$, $Li_3S_2$, $P_2S_6$, and $Li_3GeP_2S_6$ pressed pellets. The 45:2:1 refers to the relative amounts of $Li_3S_2P_2S_6Ge_2S_2$ precursors used in the synthesis.

**FIG. 13** illustrates LGPS ionic conductivity Arrhenius plot in an example according to the present invention. As shown is Arrhenius plot of the ionic conductivity of various $Li_3GeP_2S_6$ pressed pellets measured by electrochemical impedance spectroscopy with indium blocking electrodes. The ratios refer to the relative amounts of $Li_3S_2P_2S_6Ge_2S_2$ precursors used in the synthesis, while the compositions are derived from X-ray photoelectron spectroscopy measurements.

**FIG. 14** illustrates LGPS ionic conductivity as a function of P and Ge concentrations according to examples of the present invention. As shown, the ranges 5:1:1 to 15:2:1 and 45:2:1 are indicative of desirable material, and 5:1:1 is preferred, although there can be variations. Ionic conductivity of various $Li_3GeP_2S_6$ pressed pellets at 60°C measured by electrochemical impedance spectroscopy with indium blocking electrodes as a function of the $Li_3S_2P_2S_6Ge_2S_2$ precursor ratio.

**FIG. 15** illustrates composition of P and Ge in pressed pellets of $Li_3GeP_2S_6$ measured by X-ray photoelectron spectroscopy (XPS) as a function of $Li_3S_2P_2S_6Ge_2S_2$ precursor ratio. As shown, decreasing germanium and/or phosphorous content generally leads to undesirable results. Further details of the present technique can be found throughout the present specification and more particularly below.

**TABLE**

<table>
<thead>
<tr>
<th>Li</th>
<th>Ge</th>
<th>P</th>
<th>S</th>
<th>O</th>
<th>Ion conductivity (S/cm) at 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>24.94</td>
<td>6.73</td>
<td>14.47</td>
<td>46.58</td>
<td>7.29</td>
<td></td>
</tr>
<tr>
<td>52.02</td>
<td>0.10</td>
<td>0.23</td>
<td>32.46</td>
<td>8.06</td>
<td>2.5e-6</td>
</tr>
<tr>
<td>55.28</td>
<td>0.78</td>
<td>0.89</td>
<td>34.56</td>
<td>8.33</td>
<td>1e-8</td>
</tr>
<tr>
<td>62.75</td>
<td>1.92</td>
<td>0.11</td>
<td>29.93</td>
<td>8.41</td>
<td>3.5e-8</td>
</tr>
<tr>
<td>45.72</td>
<td>8.54</td>
<td>0.02</td>
<td>38.99</td>
<td>6.73</td>
<td>3e-6</td>
</tr>
</tbody>
</table>

**FIG. 16** shows the ion conductivity plotted as a function of temperature for samples according to an embodiment of the present invention. All samples were fabricated in a thermal evaporator with powder as the source material. All were made from $SiS(GeS)_2$ powder made from milling and annealing a mixture of $Li_3S_2$, $P_2S_6$, and $SiS_2$ ($GeS_2$) powders. Evaporation occurred at ~1000°C for the samples, while for other samples the temperature was gradually increased from approximately 400 to 1500°C during the course of the evaporation. The power was premixed according to the following compositions ($Li_3S_2P_2S_6SiS_2$):

<table>
<thead>
<tr>
<th>Li</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>O</th>
<th>Ion conductivity (S/cm) at 60°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.76</td>
<td>0.15</td>
<td>22.22</td>
<td>45.62</td>
<td>5.25</td>
<td>1e-7</td>
</tr>
<tr>
<td>5e-7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**FIG. 17** is an XRD spectrum of an LGPS sample with composition $Li_2.38Si_0.62P_0.08O_0.38S_1.2$ and conductivity of 9e-4 S/cm at 30°C. The peak list is presented in the following table:

<table>
<thead>
<tr>
<th>2-theta(°)</th>
<th>d(A)</th>
<th>Normalized intensity</th>
<th>FWHM(°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.38</td>
<td>7.15</td>
<td>0.08</td>
<td>0.35</td>
</tr>
<tr>
<td>14.35</td>
<td>6.17</td>
<td>0.13</td>
<td>0.50</td>
</tr>
<tr>
<td>16.05</td>
<td>5.52</td>
<td>0.13</td>
<td>1.61</td>
</tr>
<tr>
<td>16.74</td>
<td>5.29</td>
<td>0.16</td>
<td>0.35</td>
</tr>
<tr>
<td>19.55</td>
<td>4.54</td>
<td>0.06</td>
<td>0.35</td>
</tr>
<tr>
<td>20.22</td>
<td>4.39</td>
<td>0.21</td>
<td>0.38</td>
</tr>
<tr>
<td>20.91</td>
<td>4.24</td>
<td>0.07</td>
<td>0.35</td>
</tr>
<tr>
<td>24.03</td>
<td>3.70</td>
<td>0.16</td>
<td>0.40</td>
</tr>
<tr>
<td>25.27</td>
<td>3.52</td>
<td>0.21</td>
<td>0.15</td>
</tr>
<tr>
<td>26.94</td>
<td>3.31</td>
<td>0.35</td>
<td>0.28</td>
</tr>
<tr>
<td>29.10</td>
<td>3.07</td>
<td>0.30</td>
<td>0.20</td>
</tr>
<tr>
<td>29.67</td>
<td>3.01</td>
<td>1.00</td>
<td>0.34</td>
</tr>
<tr>
<td>31.15</td>
<td>2.87</td>
<td>0.16</td>
<td>0.26</td>
</tr>
<tr>
<td>31.89</td>
<td>2.80</td>
<td>0.31</td>
<td>1.44</td>
</tr>
<tr>
<td>32.37</td>
<td>2.76</td>
<td>0.08</td>
<td>0.20</td>
</tr>
<tr>
<td>33.42</td>
<td>2.68</td>
<td>0.19</td>
<td>0.43</td>
</tr>
<tr>
<td>34.12</td>
<td>2.63</td>
<td>0.09</td>
<td>0.35</td>
</tr>
<tr>
<td>36.81</td>
<td>2.44</td>
<td>0.09</td>
<td>0.35</td>
</tr>
<tr>
<td>37.86</td>
<td>2.37</td>
<td>0.13</td>
<td>0.40</td>
</tr>
<tr>
<td>41.75</td>
<td>2.16</td>
<td>0.13</td>
<td>0.51</td>
</tr>
<tr>
<td>42.52</td>
<td>2.12</td>
<td>0.09</td>
<td>0.39</td>
</tr>
<tr>
<td>44.70</td>
<td>2.03</td>
<td>0.12</td>
<td>0.27</td>
</tr>
<tr>
<td>47.73</td>
<td>1.90</td>
<td>0.23</td>
<td>0.47</td>
</tr>
<tr>
<td>51.22</td>
<td>1.78</td>
<td>0.16</td>
<td>0.21</td>
</tr>
<tr>
<td>2θ (°)</td>
<td>d (Å)</td>
<td>Normalized intensity</td>
<td>FWHM (°)</td>
</tr>
<tr>
<td>--------</td>
<td>-------</td>
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</tr>
<tr>
<td>52.09</td>
<td>1.75</td>
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<td>0.26</td>
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<tr>
<td>53.03</td>
<td>1.73</td>
<td>0.11</td>
<td>0.41</td>
</tr>
</tbody>
</table>

[0107] A solid-catholyte material may be fabricated by physical vapor deposition (PVD), chemical vapor deposition (CVD), atomic layer deposition (ALD), and solid state reaction of powders, mechanical milling of powders, solution synthesis, evaporation, or any combination thereof. It may then be mixed with the active material in a mixer or mill or with different configurations of physical vapor deposition, optionally mixed with carbon, and coated onto a substrate by calendaring, doctor blading, slot die coating, or with a standard technique as described above. It also may be coated directly on the active material with a vapor phase growth, liquid phase growth, deposition on particles in a fluidized bed, etc. Of course, there are various alternatives, modifications, and new ways of forming catholyte/Li interfaces.

[0108] This approach enables lower cost, higher energy density batteries with better temperature performance, enhanced safety, and improved electrochemical cycling stability.

[0109] The incorporation of Si lowers the total cost of the cathode by a factor of 10x compared to using Ge.

[0110] Use of Si in place of Ge appears to improve the stability of the catholyte/Li interface.

[0111] A method according to an example of the present invention can be outlined as follows:

[0112] 1. Provide a substrate member,

[0113] 2. Form a major active region comprising a plurality of first active regions spatially disposed within a cathode region such that the major active region expands or contracts from a first volume to a second volume during a period of charge and discharge;

[0114] 3. Form a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions. In an embodiment, the catholyte material comprises a lithium, metal, phosphorous, and sulfur ("LiPSO") containing material configured in a polycrystalline state;

[0115] 4. Optionally form a protective material formed overlying exposed regions of the cathode material to substantially maintain the sulfur species within the catholyte material;

[0116] 5. Form cathode active material, electron conductive additive, binder, and other elements;

[0117] 6. Mix cathode components together with a solvent into a slurry and deposit the slurry on said substrate; dry the substrate;

[0118] 7. Complete solid state battery device;

[0119] 8. Package battery device; and


[0121] The above sequence of steps is an example of a method for fabricating a battery device. In an example, steps can be combined, removed, or include others, among variations. Other variations, alternatives, and modifications can exist. Further details of these process steps can be found throughout the present specification.

[0122] Certain Embodiments of the Invention Described Herein

[0123] In one example, the present invention provides an energy storage device comprising a cathode region, the cathode region comprising a major active region comprising a plurality of first active regions spatially disposed within the cathode region, the major active region expanding or contracting from a first volume to a second volume during a period of charge and discharge; a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LiPSO") containing material configured in a polycrystalline state; an oxygen species configured within the LiPSO containing material, the oxygen species having a ratio to the sulfur species of 1:2 and less to form a LiPSO material; and a protective material forming overlying exposed regions of the cathode material to substantially maintain the sulfur species within the catholyte material. In certain embodiments, the oxygen species is less than 20 percent of the LiPSO material. In some embodiments, the sulfur containing species ranges from about 20 to 60 percent of the LiPSO material. In other embodiments, the confinement material is configured as a barrier material. In other embodiments, the confinement material substantially prevents an interaction of the sulfur containing species with an element within the major active region. In yet other embodiments, the major active region is greater than about 50 percent of the cathode region; and the catholyte material is less than about 20 percent of the cathode region. In other embodiments, the confinement material is configured to selectively allow a lithium species to traverse through the confinement material, the confinement materials comprising a plurality of spatial openings to allow the lithium species to traverse through the confinement material. In yet other embodiments, the catholyte material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogeneous thickness of material defining the cathode region.

[0124] In some examples, the present invention further comprises a polymer material configured within a vicinity of the catholyte material, the polymer material comprising a lithium species. In some of these embodiments, the polymer material is formed overlying the catholyte material, the polymer material comprising a lithium material. In other embodiments, the polymer material configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction. In some examples, the plurality of active regions has a size ranging from about first dimension to about a second dimension. In some examples, the catholyte material comprising a plurality of clusters, each of which is separable. In some other examples, the catholyte material comprising a plurality of shell structures. In yet other embodiments, the catholyte material is configured as a plurality of particles. In some examples, the present invention provides a device further comprising a second confinement material overlying each of the plurality of active regions.

[0125] In another example, the present invention provides an energy storage device comprising a cathode region, the cathode region comprising: a major active region comprising a plurality of first active regions spatially disposed within the cathode region; a catholyte material spatially
confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state; an oxygen species configured within the LGPS or LSPS containing material, the oxygen species having a ratio to the sulfur species of 1:2 and less to form a LGPSO or LSPSO material; and a confinement material formed overlying exposed regions of the cathode active material to minimize reaction between the LGPS or LSPS containing material and the active oxygen species. In some examples, the oxygen species ranges from less than 1 percent to 20 percent of the LGPSO or LSPSO material. In other examples, the sulfur containing species ranges from about 20 to 60 percent of the LGPSO or LSPSO material. In some examples, the confinement material is configured as a barrier material. In yet other examples, the confinement material substantially prevents an interaction of the sulfur containing species with an element within the major active region. In other examples, the major active region is greater than 50 percent by volume of the cathode region. In certain examples, the confinement material is configured to selectively allow a lithium species to traverse through the confinement material. In other examples, the catholyte material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogenous thickness of material defining the cathode region.

[0125] In some examples, the devices described herein further comprise a polymer material configured within a vicinity of the catholyte material, the polymer material serving as a binder material comprising a lithium species. In other examples, the polymer material is configured overlying the catholyte material, the polymer material serving as an electrolyte. In yet other embodiments, the polymer material is configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction. In some other examples, the size distribution of active regions has a medium diameter ranging from about 20 nm to about 100 nm. In some other examples, the catholyte material comprises a plurality of shell structures around the cathode active regions. In other examples, the catholyte material is configured as a plurality of particles, each of the particles having a medium diameter ranging from about 20 nm to about 300 nm. In some other examples, the catholyte material comprises a second confinement material overlying each of the plurality of active regions. In other examples, the catholyte material is substantially free from oxygen species.

[0126] In some examples, the present invention sets forth an energy storage device comprising a cathode region, the cathode region comprising a major active region comprising a plurality of first active regions spatially disposed within the cathode region; a catholyte material configured within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state; a plurality of particles characterizing the catholyte material, each of the plurality of particles is interconnected to another via a necking arrangement, each particle having a dimension characterized by a particle diameter to neck ratio dimension ranging from 1% to greater than 100% to form a polycrystalline structure having a porosity of less than 30% of a total volume of the cathode region. In some examples, the plurality of particles in the catholyte material is substantially homogenous in a micro-scale while configured in the polycrystalline structure in a ten to one hundred micron scale. In other examples, the cathode region comprises an active material, the active material comprising iron and fluorine and/or nickel and fluorine.

[0127] In some examples, any of the devices set forth herein, the catholyte material is selected from one of Li₂S, Si₃P₉S, or Li₄Ge₄P₈S₂. In some examples, the catholyte material is provided by annealing Li₂S, P₃S₁₀, and Ge₄S₈ or Si₃P₉S at between 400-700°C for greater than about 4 hrs.

[0128] In some examples, any of the devices set forth herein, the device further comprises an oxygen species configured within the LGPS or LSPS containing material, the oxygen species having a ratio to the sulfur species of 1:10 and less to form a LGPSO or LSPSO material; and a confinement material formed overlying exposed regions of the cathode active material to minimize reaction between the LGPS or LSPS containing material and the active material. In some examples, the oxygen species is less than 20 percent of the LGPSO or LSPSO material. In certain examples, the confinement material is configured as a barrier material. In yet other examples, the confinement material substantially prevents an interaction of the sulfur containing species with an element within the major active region. In other examples, the major active region is greater than 50 percent by volume of the cathode region. In certain other examples, the confinement material is configured to selectively allow a lithium species to traverse through the confinement material. In some examples, the catholyte material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogenous thickness of material defining the cathode region. In other examples, the device further comprises a polymer material configured within a vicinity of the catholyte material, the polymer material serving as an electrolyte. In yet other embodiments, the polymer material is configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction. In some examples, each of the plurality of active regions has a medium diameter ranging from about 20 nm to about 10 μm. In some examples, each of the plurality of active regions has a medium diameter ranging from about 20 nm to about 3 μm. In other examples, the catholyte material comprises a plurality of clusters, the size distribution of which has a medium diameter ranging from about 10 nm to about 300 nm. In some examples, the catholyte material comprises a plurality of shell structures around the cathode active regions. In some examples, the catholyte material is configured as a plurality of particles, the size distribution of the particles having a medium diameter ranging from about 20 nm to about 300 nm. In some other
examples, the device further comprises a second confinement material overlaying each of the plurality of active regions. In other examples, the catholyte material is substantially free from oxygen species.

[0129] In some examples, the present invention sets forth an energy storage device comprising a catholyte material spatially confined within a spatial region of the energy storage device, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material or a lithium, silicon phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline, nanocrystalline or amorphous state; a room temperature ionic conductivity ranging from $10^{-2}$ to $5\times10^{-5}$ S/cm characterizing the LGPS or LSPS material; and an electrical conductivity less than $10^{-5}$ S/cm characterizing the LGPS or LSPS material. In some examples, the room temperature ionic conductivity ranges from $10^{-2}$ to $1\times10^{-2}$ S/cm; and the electrical conductivity is less than $10^{-5}$ S/cm. In some embodiments, the device further comprises a plurality of particles characterizing the catholyte material, each of the plurality of particles is interconnected to another via a necking arrangement, each particle having a dimension characterized by a particle diameter to neck ratio dimension ranging from 1% to greater than 100% to form a polycrystalline structure having a solid area to hole area or porosity of less than 30% of a total volume of the catholyte material. In some examples, the plurality of particles in the catholyte material is substantially homogeneous in a micro-scale while configured in the polycrystalline structure in a ten to one hundred micron scale. In some other examples, the catholyte material comprises an active material, the active material comprising iron and fluorine and/or nickel and fluorine.

[0130] In some examples, the cathode region comprises an active material, the active material comprising iron and fluorine. In some examples, the cathode region comprises an active material, the active material comprising nickel and fluorine.

[0131] In any of the examples, set forth herein, the catholyte material may be selected from one of Li$_x$SiP$_y$S$_z$, or Li$_x$GeP$_y$S$_z$. In some examples, the catholyte material is provided by annealing Li$_x$S$_y$, P$_2$S$_5$, GeS$_2$ or SiS$_2$ at between 400 and 700°C for at least 4 hrs.

[0132] In some examples, the present invention sets forth an energy storage device comprising a catholyte material spatially confined within a spatial region of the energy storage device, the catholyte material comprising: a lithium, silicon phosphorous, and sulfur ("LSPS") containing material, each of which is configured in a polycrystalline or amorphous state; a room temperature ionic conductivity ranging from $10^{-2}$ to $5\times10^{-3}$ S/cm characterizing the LSPS material; an electrical conductivity less than $1\times10^{-5}$ S/cm characterizing the LSPS material; and an XRD 20 scan with Cu Kα radiation is characterized by a first major peak between about 41 to 45° 20 and a second major peak between about 30 to 35° 20 and a third major peak between 51-54° 20. In some examples, the first major peak is higher in intensity than either the second major peak or the third major peak. In other examples, the XRD is measured in counts per second and the first major peak is higher in intensity than either the second major peak or the third major peak. In yet other examples, the device exhibits a cyclic voltammogram characterized by a current density of less than 1 mA/cm$^2$ when the voltage is swept at 10 mV/s between 0.1 to 4.5V vs Li/Li$^+$ and the sample is maintained at 30°C.

[0134] In some examples, the present invention sets forth an energy storage device comprising a cathode region, the cathode region comprising a major active region comprising a plurality of first active regions spatially disposed within the cathode region, the major active region expanding or contracting from a first volume to a second volume during a period of a charge and discharge; a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions, the catholyte material comprising a lithium, germanium, phosphorous, and sulfur ("LGPS") containing material configured in a polycrystalline state; wherein the catholyte material is characterized by an XRD as measured in counts per second characterized by a first major peak between at 41 to 45° 20, between about 30 to 35° 20; whereupon the first major peak is higher in intensity than either the second major peak or the third major peak. In some examples, the device further comprises an oxygen species configured within the LGPS containing material, the oxygen species having a ratio to the sulfur species of 1:2 and less to form a LGPSO material wherein the oxygen species is less than 20 percent of the LGPSO material. In other examples, the sulfur containing species ranges from about 25 to 60 percent of the LGPSO material. In certain examples, the device further comprises a confinement material formed overlying exposed regions of the catholyte material to substantially maintain the sulfur species within the catholyte material; wherein the confinement material is configured as a barrier material.
examples, the device further comprises a confinement material; wherein the confinement material substantially prevents an interaction of the sulfur containing species with an element within the major active region. In other examples, the major active region is greater than about 50 percent by volume of the cathode region; and the catholyte material is less than about 30 percent by volume of the cathode region.

In other examples, the device further comprises a confinement material; wherein the confinement material is configured to selectively allow a lithium species to traverse through the confinement material, the confinement materials comprising a plurality of spatial openings to allow the lithium species to traverse through the confinement material. In other examples, the catholyte material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogeneous thickness of material defining the cathode region. In yet other examples, the device further comprises a polymer material configured within a vicinity of the catholyte material, the polymer material comprising a lithium species. In other examples, the polymer material is formed overlying the examples, the catholyte material comprising a lithium species. In other examples, the polymer material configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction. In still other examples, each of the plurality of active regions has a size ranging from about first dimension to about a second dimension. In other examples, the catholyte material comprises a plurality of clusters, each of which is separable. In other examples, the catholyte material comprises a plurality of shell structures. In yet other examples, the catholyte material is configured as a plurality of particles. In yet other examples, the device further comprises a second confinement material overlying each of the plurality of active regions.

[0135] In some examples, the present invention sets forth a method for manufacturing an energy storage device comprising forming a cathode region, the cathode region comprising a major active region comprising a plurality of first active regions spatially disposed within the cathode region, the major active region expanding or contracting from a first volume to a second volume during a period of a charge and discharge; a catholyte material spatially confined within a spatial region of the cathode region and spatially disposed within spatial regions not occupied by the first active regions, the catholyte material comprising a lithium, germanium, phosphorus, and sulfur ("LGPS") containing material configured in a polycrystalline state. In some examples, the LGPS containing material comprises an oxygen species configured within the LGPS containing material, the oxygen species dehydrogenating to a sulfur species of 1:2 and react to form a LGPSO material. In some other examples, the method further comprises forming a confinement material formed overlying exposed regions of the cathode material to substantially maintain the sulfur species within the catholyte material. In still other examples, the oxygen species is less than 20 atomic percent of the LGPSO material. In other examples, the sulfur containing species ranges from about 25 to 60 percent of the LGPSO material. In other examples, the method further comprises forming a confinement material configured as a barrier material. In still other examples, the confinement material substantially prevents an interaction of the sulfur containing species with an element within the major active region. In yet other examples, the major active region is at least 50 percent by volume of the cathode region; and the catholyte material is less than about 30 percent by volume of the cathode region.

In some other examples, the method further comprises forming a confinement material configured to selectively allow a lithium species to traverse through the confinement material, the confinement materials comprising a plurality of spatial openings to allow the lithium species to traverse through the confinement material. In other examples, the catholyte material is configured to substantially fill the cathode region comprising the major active region to form a substantially homogeneous thickness of material defining the cathode region. In other examples, the catholyte material configured to accommodate an internal stress within the cathode region during the change in volume from the expansion to a contraction. In some other examples, each of the plurality of active regions has a size ranging from about first dimension to about a second dimension. In still other examples, the catholyte material comprises a plurality of clusters, each of which is separable. In some examples, the catholyte material comprises a plurality of shell structures. In yet other examples, the catholyte material is configured as a plurality of particles. In yet other examples, the method further comprises a second confinement material overlying each of the plurality of active regions.

[0136] In some examples, the present invention sets forth a solid catholyte material comprising a lithium element; a silicon element; a phosphorus element; a sulfur element; and an oxygen element; wherein the major peak is located at a peak in a position of 20-30°±1° in an X-ray diffraction measurement using a CuKα line, or at the peak of 20-33°±1° or a peak of 20-43°±1°. In some embodiments, the present invention provides a solid ion conducting material characterized by a formula Li₅Si₃P₃S₈O₄ where 2s≥8, 0.5≤β≤2.5, 4≤α≤12, δ-3, wherein any impurities are less than 10 atomic percent. In some examples, the present invention provides a solid ion conducting material comprising Li, Si, P, and S characterized by primary Raman peaks at 418±10 cm⁻¹, 383±10 cm⁻¹, 284±10 cm⁻¹, and 1614±10 cm⁻¹ when measured by a Renishaw via Raman microscope. In yet other examples, the present invention provides a solid ion conducting material that results from a reaction of x Li₂S, y SiS₂, and z P₂S₅, where 1≤x≤20 and 0.5≤z/ y≤2.

[0137] In some examples, the present invention sets forth a process for manufacture of a solid ion conducting material comprising the steps of mixing Li₂S, P₂S₅, and SiS₂ and then heating the mixture to a temperature above 400° C. for a time of greater than 3 hours.

[0138] According to an embodiment of the present invention, techniques related to a solid catholyte material having desired ion conductivity are provided. More particularly, an embodiment of the present invention provides a method and structure for a catholyte material to improve a total ionic conductivity for a cathode to allow for higher mass loading of an active material, faster charge/discharge, and a wider range of operating temperature.
Merely by way of example, the invention has been applied to solid state battery cells, although there can be other applications.

[0139] As background, poor ionic conductivity of the cathode active material in a battery imposes strong limitations to overall performance, particularly in an all solid state battery wherein a solid catholyte material is needed to enable transport of ions from the cathode to the electrolyte. By mixing the low ionic conductivity cathode active material with a high ionic conductivity ceramic cathode, we can improve overall cathode conductivity. Rate capability in a battery can be improved by increasing the volume fraction of the cathode material. To improve electronic conductivity to match the ionic conductivity, a dopant species such as carbon can be added as a third component or pre-coated onto the cathode active material. Depending on the implementation, dopant species can be selected from a tin element, an aluminum element, carbon, titanium, hafnium, cerium, and/or zirconium.

[0140] In an example, an embodiment of the present invention sets forth a solid state catholyte, lithium-silicon-tin-phosphorus-sulfide (LSTPS), which possesses Li ion conductivity of >5x10^{-3} S/cm at 60°C. The composition of the catholyte is Li6Si3Sn3P14S48. LSTPS is synthesized using starting precursor materials: Li6, 3Sn, 3P, 14Si, 8S, and by a solid state reaction procedure wherein the materials are milled together and annealed to form a crystalline material.

[0141] In an example, the high ionic conductivity solid state catholyte enables improved energy density, power density, and low temperature performance of a battery with improved safety by eliminating the use of typical flammable components. Examples of conventional techniques are described.

[0142] That is, conventional cationic ceramic sulfide ionic conductors have been proposed. These materials contain up to three cations paired with a sulfur anion. These materials may be amorphous or crystalline. These materials do not utilize an advantageous doping effect of a fourth cation, which limits the achievable ionic conductivity. Examples in the literature include: Kamaya et al., A lithium super ionic conductor, Nat. Mat. 10 (2011) 682-686. DOI: 10.1038/NMAT3066, and Murayama, et al., Material design of new lithium ionic conductor, thio-LISICON, in the Li2S-P2S5 system, Solid State Ionics 170 (2004) 173-180. DOI: 10.1016/j.ssi.2004.02.025.

[0143] Conventional ceramic oxide ionic conductors have also been proposed. These ceramic oxide ionic conductors contain multiple cations paired with an oxygen anion. These materials cannot be used as catholyte materials since the space-filling requirement of the catholyte morphology needed to achieve high volumetric and gravimetric energy density necessitates a tortuous and highly granular structure with a high surface area to volume ratio. In the case of these oxides, high grain boundary impedances severely limit overall ionic conductivity, which are difficult to mitigate without high temperature sintering in excess of 1000°C. Such conditions can damage other components of the cell architecture. Examples include:

[0144] Buschmann, et al. Lithium metal electrode kinetics and ionic conductivity of the solid lithium ion conductors Li1+2/3La2/3Zr2/3O5-x and Li1+2/3La2/3Zr1/3O5-x. J. Power Sources 206 (2012) 236-244. DOI: 10.1016/j.jpowsour.2012.01.094; and


[0146] Conventional liquid ionic conductors have also been proposed. These materials typically consist of an ionic salt solvated in a liquid phase. These conductors often suffer from voltage instability. This voltage instability manifests in the formation of a solid electrode interface (SEI), which requires costly formation cycling and initial charge loss. Also extremely detrimental is the inherent flammability of these liquids, which severely impacts the overall safety of the device.

[0147] In an example, the composite ceramic catholyte material with chemical formula Li1–xX2–xP2S5 (Li1–xXPS), where X can be Ge, Si, Sn, or any combination thereof, may be synthesized using a solid state reaction. The precursors include Li6S, P2S5, an elemental powder of X, and S. The powders are mixed in a ratio (1–x)XnP2S5 where a=5, b=1, c=1, and d=2. In the case of LSPS, LTPS, or LGPS, b=1, and X is elemental Si powder (LSiPS), elemental tin powder (LTPS), or elemental germanium powder (LGPS). In a non-limiting example of LSTPS, the composition Li6Si3Sn3P14S48, where a=5, b=0.5, c=0.5, d=1, and e=2. The precursor powders are exposed to high energy planetary milling, followed by annealing in enclosed reactors at 550°C for 8 hours. The catholyte is then mixed with a binder, an active electrode material and an electronic conductor to form a composite positive electrode material, as illustrated in FIG. 18A. The positive electrode is then assembled into a fully functional solid state device, as illustrated in FIG. 18B.

[0148] FIG. 18A is a simplified illustration of an electrode material (including an active positive electrode material, ionic conductor, binder, and electronic conductor) according to an example of the present invention. The LMPS material forms a percolating network throughout the cathode and conducts ions to the active material with low transport losses.

[0149] FIG. 18B is a simplified illustration of a negative electrode current collector, a solid state electrolyte, and a positive electrode current collector according to an example of the present invention.

[0150] To assess ionic conductivity, the LXPS powders are pressed into pellets and studied using electrochemical impedance spectroscopy with blocking electrodes. The ionic conductivity of 4 component materials ranks in order of LGPS>LSPS>LTPS, as shown in FIG. 19, where average ionic conductivity of both LGPS and LSPS exceed 1x10^{-3} S/cm at 60°C. It is unexpectedly shown that addition of a dopant material to create LSTPS improves the conductivity by a factor of 2x relative to average LGPS and 10x relative to average LTPS. Champion samples of LSTPS possess conductivities in excess of 5x10^{-3} S/cm at 60°C. In an example, the conductivity of LSTPS exceeds the conductivity of any of the 4-component materials, and LSTPS is substantially less expensive than LGPS, since the cost of Ge is many times higher than the cost of Sn or Si.

[0151] Certain examples of the present invention surprisingly show that mixed Si/Sn doping unexpectedly results in beneficial conductivity properties.

[0152] In addition, the doped LSTPS material possesses an activation energy of 0.25 eV, lower than either LSPS (0.26 eV) or LTPS (0.28 eV), as previously shown in FIG. 20.
[0153] The conductivity trend extends down to 10° C, without the appearance of any additional grain boundary impedence, demonstrating the unique ability of sulfide materials to achieve excellent inter-grain contact without the need for high temperature sintering, unlike many oxide materials.

[0154] XRD shows that all of the materials possess a unique crystalline structure shown in FIG. 21. That is, FIG. 21 illustrates crystal structure from XRD spectra of LSTPS, LS, and LTSP according to examples according to the present invention.

[0155] XPS compositions in TABLE A confirm that LSTPS contains a mixture of both Si & Sn, whereas LS contains no Sn, and LTSP contains no Si. In an example, the composition range of LPS includes Li$_{2}$Si$_{2}$PS$_{4}$O$_{5}$ where 2a$_{1}$=12, 0.5a$_{2}$=5, 2a$_{3}$=15, and 0a$_{4}$=2. The composition range of LTSP includes Li$_{2}$SnPS$_{4}$O$_{5}$ where 2a$_{1}$=12, 0.5a$_{2}$=5, 2a$_{3}$=15, and 0a$_{4}$=2. The composition range of LSTPS includes 30-50 at % Li, 0-10 at % Si, 0-10 at % Sn, 5-15 at % P, 30-55 at % S, and 0-15 at % O.

TABLE A

<table>
<thead>
<tr>
<th>ID</th>
<th>Li</th>
<th>O</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>Sn</th>
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<tr>
<td>LSTPS</td>
<td>43</td>
<td>8</td>
<td>9</td>
<td>34</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>LTSP</td>
<td>36</td>
<td>11</td>
<td>13</td>
<td>34</td>
<td>0</td>
<td>6</td>
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<td>LTSP</td>
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<td>6</td>
<td>9</td>
<td>34</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

[0156] In an example, the unique chemical compositions of the Li & P atoms between the LPS compositions are shown in 71 Li NMR spectra of FIGS. 22A, 22B, 22C, and 22D and 31P NMR spectra of FIGS. 23A, 23B, 23C, and 23D. Table B below provides an example of chemical environment based on 71Li and 31P NMR analysis. In an example, the peak shifts are listed in Table B.

TABLE B

<table>
<thead>
<tr>
<th>Chemical environments based on 71Li and 31P NMR analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>71Li peak shifts (ppm)</td>
</tr>
<tr>
<td>LPS</td>
</tr>
<tr>
<td>LSTPS</td>
</tr>
<tr>
<td>LTSP</td>
</tr>
<tr>
<td>LGPS</td>
</tr>
</tbody>
</table>

FIG. 24 illustrates a schematic of full cell with solid state catholyte in an example according to the present invention. In an example, the LMS material is present in the cathode as the ion conductor providing ion transport to the active material throughout the cathode.

[0157] FIG. 25 is an SEM micrograph of cast film of solid state LMS according to an example of the present invention.

[0158] In contrast to previous efforts to synthesize a sulfide-based ion conductor, the addition of N cation dopants (where N=1, 2, 3...) further improves the ionic conductivity of the material relative to the N=1 composition. This is highlighted by the LSTPS composition, in which the conductivity exceeds both LS and LTSP, and additionally possesses lower activation energy than both LS and LTSP. The improved conductivity and shallower activation energy enables higher energy density, power density, and low temperature performance of a battery, while also possessing the non-flammability (improved safety) of an all solid state ion conductor.

[0159] A method according to an example of the present invention can be outlined as follows:

[0160] 1. In an example, powders of Li$_{2}$S, PS$_{2}$, elemental Si, elemental Sn, and elemental S are mixed in a 5:10:5:0. 5:2 mol ratio to produce LSTPS. Powders of Li$_{2}$S, PS$_{2}$, Sn$_{2}$, Sn$_{2}$ are mixed in a 5:10:5:0.5 mol ratio to produce LSTPS in an example, while there can be variations. Powders of Li$_{2}$S, PS$_{2}$, elemental Sn, and elemental S are mixed in a 5:1:1:2 mol ratio to produce LPS in an example. Powders of Li$_{2}$S, PS$_{2}$, Sn$_{2}$, and Sn$_{2}$ are mixed in a 5:1:1 mol ratio to produce LPS in an example. Powders of Li$_{2}$S, PS$_{2}$, elemental Si, and elemental S are mixed in a 5:1:1:2 mol ratio to produce LPS in an example. Powders of Li$_{2}$S, PS$_{2}$, and Sn$_{2}$ are mixed in a 5:1:1:2 mol ratio to produce LPS in an example.
LSPS in an example. Powders of Li₂S, P₂S₅, elemental Ge, and elemental S are mixed in a 5:1:1:2 mol ratio to produce LGPS in an example. Powders of Li₂S, P₂S₅, and GeS₂ are mixed in a 5:1:1 mol ratio to produce LGPS in an example. In an example, P₂S₅ can be replaced with a 2:5 mixture of elemental P and elemental S. In an example, the molar equivalent of Li₂S can be as low as 4.5 and as high as 5.5. In an example, the molar equivalent of P₂S₅ can be as low as 0.6 and as high as 1.4. In an example, the Si/(Si+Sn) stoichiometry can be as low as 0.25 and as high as 0.75. Of course, there can be variations in compositions, times, and other parameters. Depending on the specific process performed, the mixing ratios may be changed due to material loss and/or other factors.

[0161] 2. The mixture of powder from Step 1 is loaded into, for example, a 50-500 ml milling jar containing 1-10 mm spherical milling media. The milling jar and media could be composed of stainless steel, hardened steel, alumina, or zirconia, in an example. In an example, 14 gr. of the mixture from Step 1 is loaded into a 50 ml ZrO₂ milling jar containing 50 gr. of 1 mm ZrO₂ spherical milling media.

[0162] 3. The mixture in the milling jar is milled. In an example, the mixture is milled at 200-400 rpm for 4-16 hours in a planetary mill, although there can be variations, with 400 rpm for 8 hours being one preferred example. In another example, a shaker mill could be used.

[0163] 4. The powder in the milling jars from Step 3 is recovered using a sieve, preferably 80 mesh, in an example.

[0164] 5. The powder after sieving in Step 4 is loaded into an enclosed reactor. This reactor can be a vacuum sealed quartz tube or a high pressure and high temperature autoclave constructed of steel in an example.

[0165] 6. The reactor vessel is heated to 400-700°C for a soak duration of 1-8 hours.

[0166] 7. The powder after annealing in Step 6 is recovered from the reactor vessel and finely distributed using a mortar & pestle, additional planetary milling, or vortex milling in an example.

[0167] 8. The powder from Step 7 can be further downsized as needed using a planetary mill, a media mill, or a jet mill in order to achieve better percolation in a cathode in an example.

[0168] 9. The powder derived from either Step 7 or Step 8 is then mixed with an active material to form a full cathode.

[0169] 10. The cathode can then be assembled with an electrolyte and anode to create a full cell, in an example.

[0170] The above sequence of steps is an example of a method for fabricating a battery device. In an example, steps can be combined, removed, or include others, among variations. Other variations, alternatives, and modifications can exist.

[0171] In an example, a doped LSPS material is provided. In an example, the LSPS material comprises a lithium species, a silicon species, a phosphorous species, and a sulfur species. In an example, the doped LSPS material is configured with a plurality of dopant species consisting of a tin species to form an LGPS alloy material; wherein the lithium species ranges from 30 to 50 at%; wherein the silicon species ranges from 0 to 15 at%; wherein the tin species ranges from 0 to 15 at%; the phosphorous species ranges from 5 to 17 at%; the sulfur species ranges from 30-55 at%; and the oxygen species ranges from 0-15 at%.

[0172] In an example, a doped LGPS material comprising a lithium species, a germanium species, a phosphorous species, and a sulfur species is provided. The doped LGPS material is doped with a plurality of tin species to form an LGPS alloy material; wherein the lithium species ranges from 30 to 50 at%; wherein the germanium species ranges from 30 to 50 at%; wherein the germanium species ranges from 0 to 15 at%; wherein the tin species ranges from 0 to 15 at%; the phosphorous species ranges from 5 to 17 at%; the sulfur species ranges from 30 to 55 at%; and the oxygen species ranges from 0-15 at%.

[0173] In an alternative example, a doped LGPS material comprising a lithium species, a germanium species, a phosphorous species, and a sulfur species is provided. In an example, the doped LGPS material is configured with a plurality of dopant species to form an LGPS alloy material; wherein the lithium species ranges from 30 to 50 at%; wherein the germanium species ranges from 0 to 15 at%; wherein the silicon species ranges from 0 to 15 at%; wherein the phosphorous species ranges from 5 to 17 at%; and the oxygen species ranges from 0-15 at%.

[0174] In an alternative example, a doped LMPS material characterized with a plurality of different XRD peaks in a plurality of ranges including 18-21°, 26-28°, 28-31°, and 46-48° is provided. In an alternative example, a doped LMPS material characterized with at least one ⁷Li NMR peak shifts ranging from 0.5-1.5 ppm is provided. In an alternative example, a doped LMPS material characterized with at least one ²⁰⁷P NMR peak shifts ranging from 86-88 ppm (LSPS, LGPS, LSTPS), 92-94 ppm (LSTPS, LTPS, LGPS), 74-78 ppm (LSTPS, LTPS, LGPS), or 108-109 ppm (LTPS, LSTPS) is provided.

[0175] Although numerous examples of the invention have been illustrated and described, the invention is not so limited. Numerous modifications, variations, substitutions and equivalents will occur to those skilled in the art without departing from the spirit and scope of the present invention.

[0176] While the above is a full description of the specific embodiments, various modifications, alternative constructions and equivalents may be used. Therefore, the above description and illustrations should not be taken as limiting the scope of the present invention which is defined by the appended claims.

1-24. (canceled)

25. A catholyte material characterized by at least one ⁷Li NMR peak shift ranging from 0.5-1.15 ppm.