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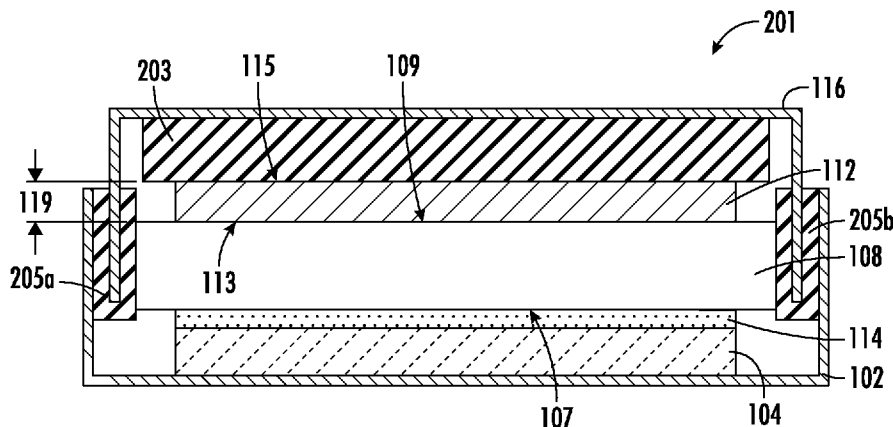


FIG. 2

(57) Abstract: Batteries include a cathode, a solid-state electrolyte, and an anode. The solid-state electrolyte has a first major surface facing the anode with a surface roughness Ra of 0.6 micrometers or less and a second major surface facing the cathode with a surface roughness Ra of 1 micrometer or more. The battery can further include a liquid electrolyte positioned between the second major surface and the anode. Methods include polishing a first major surface of a solid-state electrolyte to form surface roughness Ra of 0.6 micrometers or less. Methods include polishing a second major surface of the solid-state electrolyte to form a surface roughness Ra of 1 micrometer or more. Methods can include heating a lithium-containing precursor to form a lithium-containing anode disposed on the first major surface. Methods can include disposing the solid-state electrolyte over a cathode with the second major surface facing the cathode.



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SOLID-STATE ELECTROLYTE, BATTERIES, AND METHODS OF MAKING THE SAME

[0000] This application claims the benefit of priority of Chinese Application Serial No. 202310376946.7 filed on April 7, 2023, the content of which is relied upon and incorporated herein by reference in their entirety.

FIELD

[0001] The present disclosure relates to solid-state electrolytes, batteries, and methods of manufacturing thereof, and more particularly batteries comprising a solid-state electrolyte and methods of making the same.

BACKGROUND

[0002] Solid-state batteries (SSBs) (e.g., SS lithium (Li) metal batteries based on inorganic solid-state electrolytes (SSEs) (such as garnet-type SSE)) have attracted much attention due to their high safety, improved energy density, high ionic conductivity, and stability against Li metal. However, conventional Li-metal batteries often suffer from issues with capacity retention and/or longevity, especially when operated at higher capacities. Consequently, there is a need to address these issues.

SUMMARY

[0003] The present disclosure provides solid-state electrolytes, batteries, and methods of making the same comprising a surface(s) of the solid-state electrolyte with a predetermined surface roughness Ra. The surface roughness Ra of the first major surface (e.g., facing the anode) of the solid-state electrolyte can be about 0.6 μm or less (e.g., from about 0.1 μm to about 0.5 μm), which can increase a charging rate that the battery can withstand. The surface roughness of the second major surface (e.g., facing the cathode) of the solid-state electrolyte can be about 1 μm or more (e.g., from about 1.2 μm to about 3 μm), which can decrease an interfacial resistance of the battery. Further combining a low surface roughness Ra of the first major surface (e.g., about 0.6 μm or less or from about 0.1 μm to about 0.5 μm) with a high surface roughness Ra of the second major surface (e.g., about 1 μm or more or from about 1.2 μm to about 3 μm) can unexpectedly increase the longevity of the battery and/or the capacity retention of the battery and as demonstrated in the Examples herein. Without wishing to be bound by theory, it is believed that the low roughness (e.g., about 0.6 μm or less or from about 0.1 μm to about 0.5 μm) of the first major surface enables increased charging rates by providing a substantially uniform surface for the anode, which enables

uniform contact with the anode, reduces current concentration across the surface, and/or decreases the formation of dendrites. Without wishing to be bound by theory, it is believed that high roughness (e.g., about 1 μm or more or from about 1.2 μm to about 3 μm) of the second major surface decreases interfacial resistance by increasing a surface area of the interface between the solid-state electrolyte and the liquid electrolyte.

[0004] Methods of the present disclosure include polishing the first major surface and/or the second major surface to achieve a predetermined surface roughness R_a . The polishing can comprise etching, mechanical polishing, or a combination thereof. Without wishing to be bound by theory, etching for a short period of time (e.g., about 4 minutes or less) can reduce surface irregularities without increasing a surface roughness of the first major surface (e.g., by etching grain boundaries of the solid-state electrolytes). Without wishing to be bound by theory, etching for a short period of time (e.g., about 4 minutes or less) can reduce surface irregularities without increasing a surface roughness of the first major surface (e.g., by etching grain boundaries of the solid-state electrolytes). Without wishing to be bound by theory, etching for a longer period of time (e.g., about 7 minutes or more) can increase a surface roughness of the second major surface, for example by etching grain boundaries of the solid-state electrolytes and/or leaching portions of the solid-state electrolyte. Providing a high grit (or low median particle size) abrasive for mechanically polishing the first major surface can produce a low surface roughness of the first major surface.

[0005] Methods and batteries can comprise a lithium-containing anode. In aspects, the lithium-containing anode can be a lithium alloy, which can increase a wettability of the lithium-containing material on the first major surface of the solid-state electrolyte, which enables the battery to withstand high charging rates even when the lithium alloy is heated at 300°C as well as at greater temperatures. In aspects, the lithium-containing anode can consist essentially of lithium metal. Methods of the present disclosure comprise heating the lithium metal at about 330°C or more can enable the lithium metal to wet or otherwise conform to the first major surface, which unexpectedly improves the charging rate that the battery can withstand, as demonstrated by the Examples herein, for example, by providing intimate and/or uniform contact between the lithium metal anode and the first major surface of the solid-state electrolyte.

[0006] Providing a solid-state electrolyte (e.g., in a solid-state battery) can address common safety concerns, for example, leakage, poor chemical stability, and flammability often seen in batteries employing liquid electrolytes. Moreover, providing a solid-state electrolyte can also suppress polysulfide shuttling from the cathode to the anode, thereby leading to improved electrode (e.g., anode, cathode) utilization and a high discharge capacity and energy density.

Providing a solid-state electrolyte can reduce a formation of dendrites (e.g., lithium dendrites) that can otherwise result in failure of the battery. Providing an interlayer comprising a liquid electrolyte can wet the interface between the cathode and the solid-state electrolyte to reduce interfacial resistance therebetween while minimizing a total amount of liquid electrolyte in the solid-state battery.

[0007] Some example aspects of the disclosure are described below with the understanding that any of the features of the various aspects may be used alone or in combination with one another.

[0008] Aspect 1. A battery, comprising:

a lithium-containing anode;

a solid-state electrolyte comprising a first major surface facing the lithium-containing anode and a second major surface opposite the first major surface, and the first major surface comprising a surface roughness Ra of about 0.6 micrometers or less, and the second major surface comprising a surface roughness of about 1 micrometer or more;

a liquid electrolyte disposed on the second major surface of the solid-state electrolyte; and
a cathode disposed over the second major surface of the solid-state electrolyte, the liquid electrolyte positioned between the second major surface and the cathode.

[0009] Aspect 2. The battery of aspect 1, wherein the surface roughness Ra of the first major surface ranges from about 0.1 micrometers to about 0.5 micrometers.

[0010] Aspect 3. The battery of any one of aspects 1-2, wherein the surface roughness Ra of the second major surface ranges from about 1.2 micrometers to about 3 micrometers.

[0011] Aspect 4. The battery of any one of aspects 1-3, wherein an interfacial resistance between the cathode and the lithium-containing anode is about $60 \Omega \text{ cm}^2$ or less at 25°C .

[0012] Aspect 5. The battery of aspect 4, wherein the interfacial resistance ranges from about $10 \Omega \text{ cm}^2$ to about $40 \Omega \text{ cm}^2$.

[0013] Aspect 6. The battery of any one of aspects 1-3, wherein an interfacial resistance of the battery is about 50% or less than an interfacial resistance of another battery identical to the battery but with the first major surface and the second major surface switched.

[0014] Aspects 7. The battery of any one of aspects 1-5, wherein the battery can withstand at least 10 cycles at a charging current density of 1.6 mA/cm^2 or more to a capacity of 1 mAh/cm^2 with a discharge rate of 0.5 mA/cm^2 at 25°C , where the area is based on a surface area of the lithium-containing anode.

[0015] Aspect 8. The battery of aspect 7, wherein the battery can withstand at least 10 cycles at a charging current density of 2 mA/cm^2 to the capacity of 1 mAh/cm^2 with the discharge rate of 0.5 mA/cm^2 at 25°C .

[0016] Aspect 9. The battery of any one of aspects 7-8, wherein another battery identical to the battery but with the first major surface and the second major surface switched cannot withstand 10 cycles at a charging current density of 1.25 mA/cm^2 to the capacity of 1 mAh/cm^2 with the discharge rate of 0.5 mA/cm^2 at 25°C .

[0017] Aspect 10. The battery of any one of aspects 1-6, wherein the battery comprises a capacity retention of about 90% or more after 60 cycles at a charging rate of 0.5C and a discharging rate of 0.17 C to a maximum capacity of 3 mAh/cm^2 with a cutoff voltage of 4.5V and at 60°C , and the area is based on a surface area of the lithium-containing anode.

[0018] Aspect 11. The battery of any one of aspects 1-10, wherein the lithium-containing anode comprises an alloy of lithium and at least one of magnesium, silver, or combinations thereof.

[0019] Aspect 12. The battery of any one of aspects 1-11, wherein the cathode comprises at least one of lithium cobaltite (LCO), lithium manganite spinel (LMO), lithium nickel cobalt aluminate (NCA), lithium nickel manganese cobalt oxide (NCM) ($\text{LiNi}_d\text{Co}_e\text{Mn}_{1-d-e}\text{O}_2$, where $0 < d < 1$, $0 < e < 1$), lithium iron phosphate (LiFePO_4) (LFP), lithium cobalt phosphate (LCP), lithium titanate, lithium niobium tungstate, lithium nickel manganate, and lithium titanium sulfide (LiTiS_2), or combinations thereof.

[0020] Aspect 13. The battery of any one of aspects 1-12, wherein the solid-state electrolyte comprises lithium, lanthanum, zirconium, and oxygen.

[0021] Aspect 14. The battery of any one of aspects 1-13, wherein the solid-state electrolyte comprises at least one of:

- (i) $\text{Li}_{7-3a}\text{La}_3\text{Zr}_2\text{La}_a\text{O}_{12}$, with $L = \text{Al, Ga, or Fe}$ and $0 < a < 0.33$;
- (ii) $\text{Li}_7\text{La}_{3-b}\text{Zr}_2\text{M}_b\text{O}_{12}$, with $M = \text{Bi or Y}$ and $0 < b < 1$;
- (iii) $\text{Li}_{7-c}\text{La}_3(\text{Zr}_{2-c}\text{N}_c)\text{O}_{12}$, with $N = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < c < 1$;
- (iv) protonated LLZO (e.g., $\text{H}_x\text{Li}_{6.5-x}\text{La}_3\text{Zr}_{1.5}\text{I}_{0.5}\text{O}_{12}$, with $I = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < x < 4$ or $\text{H}_x\text{Li}_{6.25-x}\text{E}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, with $E = \text{Al, Ga, or Fe}$ and $0 < x < 4$); or a combination thereof.

[0022] Aspect 15. The battery of any one of aspects 1-14, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 20 micrometers to about 300 micrometers, and the solid-state electrolyte comprises a sintered tape.

[0023] Aspect 16. The battery of any one of aspects 1-14, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 500 micrometers and about 2 millimeters, and the solid-state electrolyte comprises consolidated pellets.

[0024] Aspect 17. The battery of any one of aspects 1-16, wherein a ratio of a weight of the cathode to a cathode surface area of the cathode ranges from about 5 mg/cm² to about 50 mg/cm².

[0025] Aspect 18. The battery of any one of aspects 1-16, wherein a ratio of a volume of the liquid electrolyte to an area of the cathode ranges from about 5 µL/cm² to about 20 µL/cm².

[0026] Aspect 19. The battery of any one of aspects 1-18, wherein the liquid electrolyte comprises a lithium salt in a solvent, the lithium salt comprises at least one of: lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), lithium perchlorate (LiClO₄), lithium tetrafluoroborate (LiBF₄), lithium triflate (LiSO₃CF₃), LiC(SO₂CF₃)₃, or combinations thereof.

[0027] Aspect 20. The battery of aspect 19, wherein the solvent comprises sulfolane, and a concentration of the lithium salt in the liquid electrolyte ranges from about 1 molar to about 3 molar.

[0028] Aspect 21. A method of forming a battery comprising:
polishing a first major surface of a solid-state electrolyte to form a surface roughness Ra of about 0.6 micrometers or less;
polishing a second major surface of the solid-state electrolyte to form a surface roughness Ra of about 1 micrometer or more, the second major surface opposite the first major surface;
heating a lithium-containing precursor at a temperature of about 300°C or more to form a lithium-containing anode disposed on the first major surface; and
disposing the solid-state electrolyte over a cathode, the second major surface of the solid-state electrolyte facing the cathode.

[0029] Aspect 22. The method of aspect 21, wherein the heating the lithium-containing precursor comprises heating at a temperature from about 330°C to about 400°C for from about 5 minutes to about 10 minutes.

[0030] Aspect 23. The method of aspect 22, wherein the lithium-containing anode consists essentially of lithium metal.

[0031] Aspect 24. The method of any one of aspects 21-22, wherein the lithium-containing anode comprises an alloy of lithium and at least one of magnesium, silver, or combinations thereof.

[0032] Aspect 25. The method of any one of aspects 21-24, wherein the polishing the first major surface comprises mechanical polishing.

[0033] Aspect 26. The method of aspect 25, wherein the mechanical polishing comprises polishing with a grit size of about 1000 or more.

[0034] Aspect 27. The method of any one of aspects 21-26, wherein polishing the second major surface comprises mechanical polishing with a grit size of about 600 or less.

[0035] Aspect 28. The method of any one of aspects 21-24, wherein the polishing the first major surface comprises etching in an acidic solution.

[0036] Aspect 29. The method of aspect 28, wherein the etching comprises contacting the first major surface with an acidic solution comprising a concentration from about 0.1 molar to about 3 molar for about 4 minutes or less.

[0037] Aspect 30. The method of any one of aspects 21-26 and 28 inclusive, wherein the polishing the second major surface comprising etching in an acidic solution comprising a concentration from about 0.1 molar to about 3 molar for from about 7 minutes to about 30 minutes.

[0038] Aspect 31. The method of any one of aspects 21-30, further comprising disposing a liquid electrolyte on the cathode such that the liquid electrolyte is positioned between the cathode and the second major surface, the liquid electrolyte comprising a lithium-containing salt.

[0039] Aspect 32. The method of aspect 31, wherein the solvent comprises sulfolane, and a concentration of the lithium salt in the liquid electrolyte ranges from about 1 molar to about 3 molar.

[0040] Aspect 33. The method of any one of aspects 21-32, wherein the surface roughness Ra of the first major surface ranges from about 0.1 micrometers to about 0.5 micrometers.

[0041] Aspect 34. The method of any one of aspects 21-33, wherein the surface roughness Ra of the second major surface range from about 1.2 micrometers to about 3 micrometers.

[0042] Aspect 35. The method of any one of aspects 21-34, wherein an interfacial resistance between the cathode and the lithium-containing anode is about $60 \Omega \text{ cm}^2$ or less at 25°C .

[0043] Aspect 36. The method of any one of aspects 21-34, wherein an interfacial resistance of the battery is about 50% or less than an interfacial resistance of another battery identical to the battery but with the first major surface and the second major surface switched.

[0044] Aspect 37. The method of any one of aspects 21-36, wherein the battery can withstand at least 10 cycles at a charging current density of 1.6 mA/cm^2 or more to a capacity of 1 mAh/cm^2 with a discharge rate of 0.5 mA/cm^2 at 25°C , where the area is based on a surface area of the lithium-containing anode.

[0045] Aspect 38. The method of aspect 37, wherein the battery can withstand at least 10 cycles at a charging current density of 2 mA/cm^2 to the capacity of 1 mAh/cm^2 with the discharge rate of 0.5 mA/cm^2 at 25°C .

[0046] Aspect 39. The method of any one of aspects 37-38, wherein another battery identical to the battery but with the first major surface and the second major surface switched cannot withstand 10 cycles at a charging current density of 1.25 mA/cm^2 to the capacity of 1 mAh/cm^2 with the discharge rate of 0.5 mA/cm^2 at 25°C .

[0047] Aspect 40. The method of any one of aspects 21-36, wherein the battery comprises a capacity retention of about 90% or more after 60 cycles at a charging rate of 0.5C and a discharging rate of 0.17C to a maximum capacity of 3 mAh/cm^2 with a cutoff voltage of 4.5V and at 60°C , and the area is based on a surface area of the lithium-containing anode.

[0048] Aspect 41. The method of any one of aspects 21-40, wherein the cathode comprises at least one of lithium cobaltite (LCO), lithium manganite spinel (LMO), lithium nickel cobalt aluminate (NCA), lithium nickel manganese cobalt oxide (NCM) ($\text{LiNi}_d\text{Co}_e\text{Mn}_{1-d-e}\text{O}_2$, where $0 < d < 1$, $0 < e < 1$), lithium iron phosphate (LiFePO_4) (LFP), lithium cobalt phosphate (LCP), lithium titanate, lithium niobium tungstate, lithium nickel manganate, and lithium titanium sulfide (LiTiS_2), or combinations thereof.

[0049] Aspect 42. The method of any one of aspects 21-41, wherein the solid-state electrolyte comprises at least one of:

- (i) $\text{Li}_{7-3a}\text{La}_3\text{Zr}_2\text{La}_a\text{O}_{12}$, with $\text{L} = \text{Al, Ga, or Fe}$ and $0 < a < 0.33$;
- (ii) $\text{Li}_7\text{La}_{3-b}\text{Zr}_2\text{M}_b\text{O}_{12}$, with $\text{M} = \text{Bi or Y}$ and $0 < b < 1$;
- (iii) $\text{Li}_{7-c}\text{La}_3(\text{Zr}_{2-c}\text{N}_c)\text{O}_{12}$, with $\text{N} = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < c < 1$;
- (iv) protonated LLZO (e.g., $\text{H}_x\text{Li}_{6.5-x}\text{La}_3\text{Zr}_{1.5}\text{I}_{0.5}\text{O}_{12}$, with $\text{I} = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < x < 4$ or $\text{H}_x\text{Li}_{6.25-x}\text{E}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, with $\text{E} = \text{Al, Ga, or Fe}$ and $0 < x < 4$); or a combination thereof.

[0050] Aspect 43. The method of any one of aspects 21-42, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 20 micrometers to about 300 micrometers, and the solid-state electrolyte comprises a sintered tape.

[0051] Aspect 44. The method of any one of aspects 21-42, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 500 micrometers and about 2 millimeters, and the solid-state electrolyte comprises consolidated pellets.

[0052] Aspect 45. The method of any one of aspects 21-44, wherein a ratio of a weight of the cathode to a cathode surface area of the cathode ranges from about 5 mg/cm² to about 50 mg/cm².

[0053] Aspect 46. The method of any one of aspects 21-44, wherein a ratio of a volume of the liquid electrolyte to an area of the cathode ranges from about 5 μL/cm² to about 20 μL/cm².

[0054] Aspect 47. A solid-state electrolyte comprising:
a body comprising a garnet-based material;
a first major surface of the body, the first major surface comprising a surface roughness Ra of about 0.6 micrometers or less; and
a second major surface of the body opposite the first major surface, the second major surface comprising a surface roughness of about 1 micrometer or more.

[0055] Aspect 48. The battery of aspect 47, wherein the surface roughness Ra of the first major surface ranges from about 0.1 micrometers to about 0.5 micrometers.

[0056] Aspect 49. The battery of any one of aspects 47-48, wherein the surface roughness Ra of the second major surface range from about 1.2 micrometers to about 3 micrometers.

[0057] Aspect 50. The battery of any one of aspects 47-49, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 20 micrometers to about 300 micrometers, and the solid-state electrolyte comprises a sintered tape.

[0058] Aspect 51. The battery of any one of aspects 47-50, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 500 micrometers and about 2 millimeters, and the solid-state electrolyte comprises consolidated pellets.

[0059] Aspect 52. A method of treating a solid-state electrolyte:
polishing a first major surface of the solid-state electrolyte to form a surface roughness Ra of about 0.6 micrometers or less; and
polishing a second major surface of the solid-state electrolyte to form a surface roughness Ra of about 1 micrometer or more, the second major surface opposite the first major surface.

[0060] Aspect 53. The method of aspect 52, wherein the polishing the first major surface comprises mechanical polishing.

[0061] Aspect 54. The method of aspect 53, wherein the mechanical polishing comprises polishing with a grit size of about 1000 or more.

[0062] Aspect 55. The method of any one of aspects 52-54, wherein polishing the second major surface comprises mechanical polishing with a grit size of about 600 or less.

[0063] Aspect 56. The method of aspect 52, wherein the polishing the first major surface comprises etching in an acidic solution.

[0064] Aspect 57. The method of aspect 56, wherein the etching comprises contacting the first major surface with an acidic solution comprising a concentration from about 0.1 molar to about 3 molar for about 4 minutes or less.

[0065] Aspect 58. The method of any one of aspects 52-54 and 56 inclusive, wherein the polishing the second major surface comprising etching in an acidic solution comprising a concentration from about 0.1 molar to about 3 molar for from about 7 minutes to about 30 minutes.

[0066] Aspect 59. The method of any one of aspects 52-58, wherein the solid-state electrolyte comprises at least one of:

- (i) $\text{Li}_{7-3a}\text{La}_3\text{Zr}_2\text{LaO}_{12}$, with $\text{L} = \text{Al, Ga, or Fe}$ and $0 < a < 0.33$;
- (ii) $\text{Li}_7\text{La}_{3-b}\text{Zr}_2\text{MbO}_{12}$, with $\text{M} = \text{Bi or Y}$ and $0 < b < 1$;
- (iii) $\text{Li}_{7-c}\text{La}_3(\text{Zr}_{2-c}\text{N}_c)\text{O}_{12}$, with $\text{N} = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < c < 1$;
- (iv) protonated LLZO (e.g., $\text{H}_x\text{Li}_{6.5-x}\text{La}_3\text{Zr}_{1.5}\text{I}_{0.5}\text{O}_{12}$, with $\text{I} = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < x < 4$ or $\text{H}_x\text{Li}_{6.25-x}\text{E}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$, with $\text{E} = \text{Al, Ga, or Fe}$ and $0 < x < 4$); or

[0067] a combination thereof.

[0068] Aspect 60. The method of any one of aspects 52-59, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 20 micrometers to about 300 micrometers, and the solid-state electrolyte comprises a sintered tape.

[0069] Aspect 61. The method of any one of aspects 52-59, wherein a thickness of the solid-state electrolyte between the first major surface and the second major surface ranges from about 500 micrometers and about 2 millimeters, and the solid-state electrolyte comprises consolidated pellets.

BRIEF DESCRIPTION OF THE DRAWINGS

[0070] The above and other features and advantages of aspects of the present disclosure are better understood when the following detailed description is read with reference to the accompanying drawings, in which:

[0071] **FIG. 1** schematically illustrates a general structure of a solid-state battery in accordance with aspects of the disclosure;

[0072] **FIG. 2** illustrates a simplified solid-state battery with the solid-state electrolyte in accordance with aspects of the disclosure;

[0073] **FIG. 3** illustrates a step in an exemplary method comprising disposing a precursor on the solid-state electrolyte to form an anode;

[0074] **FIG. 4** illustrates a step in an exemplary method comprising heating the precursor and the solid-state electrolyte;

[0075] **FIG. 5** illustrates a step in an exemplary method comprising disposing a liquid electrolyte over a cathode;

[0076] **FIG. 6** illustrates a step in an exemplary method comprising disposing the solid-state electrolyte over the cathode;

[0077] **FIG. 7** illustrates a step in an exemplary method comprising etching the first major surface of the solid-state electrolyte;

[0078] **FIG. 8** illustrates a step in an exemplary method comprising etching the second major surface of the solid-state electrolyte;

[0079] **FIG. 9** illustrates a step in an exemplary method comprising mechanically polishing the first major surface of the solid-state electrolyte;

[0080] **FIG. 10** illustrates a step in an exemplary method comprising mechanically polishing the second major surface of the solid-state electrolyte;

[0081] **FIG. 11** schematically illustrates a scanning electron microscope (SEM) images of Examples A-D;

[0082] **FIG. 12.** Illustrates a Nyquist plots for Example 1 and Comparative Examples AA-CC;

[0083] **FIG. 13** illustrates a Nyquist plots for Example 2 and Comparative Examples DD-FF;

[0084] **FIG. 14** illustrates capacity-voltage (CV) curves for Comparative Example AA;

[0085] **FIG. 15** illustrates CV curves for Example 1;

[0086] **FIG. 16** illustrates CV curves for Comparative Example BB;

- [0087] FIG. 17 illustrates CV curves for Comparative Example CC;
[0088] FIG. 18 illustrates CV curves for Comparative Example DD;
[0089] FIG. 19 illustrates CV curves for Example 2;
[0090] FIG. 20 illustrates CV curves for Comparative Example EE;
[0091] FIG. 21 illustrates CV curves for Comparative Example FF;
[0092] FIG. 22 illustrates a Nyquist plots for Example 3 and Comparative Examples GG-HH;
[0093] FIG. 23 illustrates the capacity retention of Example 3 and Comparative Examples GG-HH;
[0094] FIG. 24 illustrates CV curves for Example 4;
[0095] FIG. 25 illustrates CV curves for Comparative Example II;
[0096] FIG. 26 illustrates CV curves for Comparative Example JJ; and
[0097] FIG. 27 illustrates CV curves for Comparative Example KK.

[0098] Throughout the disclosure, the drawings are used to emphasize certain aspects. As such, it should not be assumed that the relative size of different regions, portions, and substrates shown in the drawings are proportional to its actual relative size, unless explicitly indicated otherwise.

DETAILED DESCRIPTION

[0099] Aspects will now be described more fully hereinafter with reference to the accompanying drawings in which example aspects are shown. Whenever possible, the same reference numerals are used throughout the drawings to refer to the same or like parts.

[0100] FIGS. 1-2 illustrate views of a solid-state battery **101 or 201** comprising a solid-state electrolyte with a predetermined surface roughness R_a for a first major surface **109** and/or a second major surface **107**. In aspects, the surface roughness R_a of the second major surface **107** can be greater than the surface roughness R_a of the first major surface **109**. In aspects, the surface roughness R_a of the first major surface **109** can be about $0.6\ \mu\text{m}$ or less (e.g., from about $0.1\ \mu\text{m}$ to about $0.5\ \mu\text{m}$), and/or the surface roughness R_a of the second major surface **107** can be about $1\ \mu\text{m}$ or more (e.g., from about $1.2\ \mu\text{m}$ to about $3\ \mu\text{m}$). Unless otherwise noted, a discussion of features of aspects of one solid-state electrolyte or battery can apply equally to corresponding features of any aspects of the disclosure. For example, identical part numbers throughout the disclosure can indicate that, in some aspects, the identified features are identical to one another and that the discussion of the identified feature of one aspect, unless otherwise noted, can apply equally to the identified feature of any of the other aspects of the disclosure.

[0101] FIG. 1 schematically illustrates a general structure of a solid-state battery 101, and FIG. 2 illustrates a simplified solid-state battery 201 in a coin-cell form. As shown in FIG. 1, the solid-state battery 101 or 201 can include, sequentially, a first current collector 102 (e.g., substrate), a cathode 104 disposed on the first current collector 102, an optional interlayer 114 disposed on the cathode 104, an optional first coating 106, the solid-state electrolyte 108, an optional second interlayer or coating 110, and the anode 112, and a second current collector 116 disposed on the anode 112. As shown in FIG. 1, the solid-state battery 101 can optionally comprise the optional first coating 106 positioned between the cathode 104 and the solid-state electrolyte 108, and/or the solid-state battery 101 can optionally comprise the optional second interlayer or coating 110 positioned between the anode 112 and the solid-state electrolyte 108. As shown in FIGS. 1-2, the solid-state electrolyte 108 is positioned between the cathode 104 and the anode 112. The components of the solid-state battery 101 can be disposed horizontally in relation to each other or vertically.

[0102] The first current collector 102 comprises an electrically conductive material. As used herein, electrically conductive materials have an electronic conductivity of 100 Siemens per meter (S/m) measured at 20°C in accordance with ASTM E1004-17. In aspects, the first current collector can comprise nickel (Ni) foam, carbon fiber, or a solid metal contact (e.g., aluminum, stainless steel, copper, platinum, nickel, gold, zinc, cobalt, nickel, ruthenium, lithium, lead, titanium, nichrome, etc.). In aspects, the first current collector 102 can be a mechanically stable and/or dimensionally stable substrate that supports the other elements of the solid-state battery 101 or 201. In aspects, the first current collector 102 can comprise the same material as the cathode 104 (discussed below) such that the first current collector 102 is part of the cathode 104.

[0103] The cathode 104 comprises an electrically conductive material. In aspects, the cathode 104 can be configured to release and reincorporate a cation (e.g., alkali metal – lithium or sodium, alkali earth metal – magnesium or calcium). In aspects, the cathode 104 can comprise at least one of an alkali metal (e.g., lithium, sodium) or an alkaline earth metal (e.g., magnesium, calcium). In aspects, the cathode 104 can comprise one or more of the materials discussed below for the anode 112. In further aspects, the cathode 104 can comprise the same material as the anode 112. In aspects, the cathode 104 can comprise a fluoride compound. In further aspects, the cathode 104 can comprise at least one transition metal, for example, cobalt, manganese, nickel, niobium, tantalum, vanadium, titanium, copper, chromium, tungsten, molybdenum, tin, germanium, antimony, bismuth, iron, or combinations thereof. In aspects, the cathode 104 can comprise a lithium-based electrode, for example lithium cobaltite (LCO), lithium manganite spinel (LMO),

lithium nickel cobalt aluminate (NCA), lithium nickel manganese cobalt oxide (NCM) ($\text{LiNi}_d\text{Co}_e\text{Mn}_{1-d-e}\text{O}_2$, where $0 < d < 1$, $0 < e < 1$, for example, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ (NCM523), $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ (NCM622), etc.), lithium iron phosphate (LiFePO_4) (LFP), lithium cobalt phosphate (LCP), lithium titanate, lithium niobium tungstate, lithium nickel manganate, lithium titanium sulfide (LiTiS_2), or combinations thereof. In aspects, the cathode **104** can comprise a sodium-based electrode, for example, NaVPO_4F , NaMnO_2 , $\text{Na}_{2/3}\text{Mn}_{1-y}\text{Mg}_y\text{O}_2$ ($0 < y < 1$), $\text{Na}_2\text{Li}_2\text{Ti}_5\text{O}_{12}$, $\text{Na}_2\text{Ti}_3\text{O}_7$, or combinations thereof. In aspects, the cathode **104** can comprise a magnesium-based electrode, for example, magnesiochromite (MgCr_2O_4), MgMn_2O_4 , or combinations thereof. The cathode **104** can be a sintered electrode. Alternatively, the cathode **104** can be unsintered. An exemplary aspect of a cathode **104** is a NCM cathode. In aspects, a ratio of a weight of the cathode **104** to a cathode surface area (e.g., first major surface **105** of the cathode **104** shown in **FIGS. 5-6**) of the cathode **104** can be about 5 milligrams per centimeter squared (mg/cm^2), about 8 mg/cm^2 or more, about 10 mg/cm^2 or more, about 15 mg/cm^2 or more, about 20 mg/cm^2 or more, about 50 mg/cm^2 or less, about 30 mg/cm^2 or less, about 25 mg/cm^2 or less, about 20 mg/cm^2 or less, or about 15 mg/cm^2 or less. In aspects, a ratio of a weight of the cathode **104** to a cathode surface area of the cathode **104** can range from about 5 mg/cm^2 to about 50 mg/cm^2 , from about 8 mg/cm^2 to about 30 mg/cm^2 , from about 10 mg/cm^2 to about 25 mg/cm^2 , from about 15 mg/cm^2 to about 20 mg/cm^2 , or any range or subrange therebetween.

[0104] As shown in **FIG. 1**, the solid-state battery **101** can optionally comprises an interlayer **114** positioned between the cathode **104** and the solid-state electrolyte **108**. In aspects, the interlayer **114** can comprise a liquid electrolyte (e.g., ionic liquid, deep eutectic solvent (DES), or an aprotic solvent). As used herein, an “electrolyte” enables the transport of ions therein (“ion conductivity”), and the ion conductivity corresponds to an electrical conductivity of the electrolyte (e.g., DES-based electrolyte). The interlayer **114** can be a liquid at room temperature (i.e., 25°C) and/or at an operating temperature of the solid-state battery **101** (e.g., from about 50°C to about 60°C). In aspects, the liquid electrolyte can comprise a lithium-containing salt and a solvent. In further aspects, the lithium-containing salt can comprise one or more of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), lithium perchlorate (LiClO_4), lithium tetrafluoroborate (LiBF_4), lithium triflate (LiSO_3CF_3), $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, or combinations thereof. In further aspects, a concentration of the lithium-containing salt can be about 0.5 molar (M) or more, about 1 M or more, about 1.2 M or more, about 1.5 M or more, about 3 M or less, about 2.5 M or less, or about 2 M or less, for example, in a range from about 0.5 M to about 3 M, from about 1 M to about 3 M, from about 1.2 M to about 2.5 M, from about 1.5 M to

about 2 M, or any range or subrange therebetween. An exemplary aspect of the solvent is sulfolane, although other solvents are possible in other aspects. Providing an interlayer **114** comprising a liquid electrolyte can wet the interface between the cathode **104** and the solid-state electrolyte to reduce interfacial resistance therebetween while minimizing a total amount of liquid electrolyte in the solid-state battery **101**. In aspects, a volume of the liquid electrolyte of the interlayer **114** to a cathode surface area (e.g., first major surface **105** of the cathode **104** shown in **FIGS. 5-6**) of the cathode **104** can be about 5 $\mu\text{L}/\text{cm}^2$ or more, about 8 $\mu\text{L}/\text{cm}^2$ or more, about 10 $\mu\text{L}/\text{cm}^2$ or more, about 12 $\mu\text{L}/\text{cm}^2$ or more, about 15 $\mu\text{L}/\text{cm}^2$ or more, about 20 $\mu\text{L}/\text{cm}^2$ or less, about 15 $\mu\text{L}/\text{cm}^2$ or less, about 12 $\mu\text{L}/\text{cm}^2$ or less, or about 10 $\mu\text{L}/\text{cm}^2$ or less. In aspects, a volume of the liquid electrolyte of the interlayer **114** to a cathode surface area of the cathode **104** can range from about 5 $\mu\text{L}/\text{cm}^2$ to about 20 $\mu\text{L}/\text{cm}^2$, from about 8 $\mu\text{L}/\text{cm}^2$ or to about 15 $\mu\text{L}/\text{cm}^2$ or, from about 10 $\mu\text{L}/\text{cm}^2$ to about 12 $\mu\text{L}/\text{cm}^2$, or any range or subrange therebetween.

[0105] As shown in **FIGS. 1-2**, the solid-state battery **101** and **201** comprises the solid-state electrolyte **108** positioned between the cathode **104** and the anode **112**. Throughout the disclosure, “solid-state batteries” comprise a solid-state electrolyte. As used herein, a solid-state electrolyte is a material that is solid at room temperature and at an operating temperature (e.g., about 50°C) of the solid-state battery. In aspects, the solid-state electrolyte **108** can comprise an inorganic solid-state electrolyte. Providing a solid-state electrolyte can address common safety concerns, for example, leakage, poor chemical stability, and flammability often seen in batteries employing liquid electrolytes. Moreover, providing a solid-state electrolyte can also suppress polysulfide shuttling from the cathode to the anode, thereby leading to improved electrode (e.g., anode, cathode) utilization and a high discharge capacity and energy density. Providing a solid-state electrolyte can reduce a formation of dendrites (e.g., lithium dendrites) that can otherwise result in failure of the battery.

[0106] In aspects, the solid-state electrolyte **108** can comprise a lithium-phosphorous-oxynitride (LiPON), lithium garnet ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$), lithium phosphosulfide, or combinations thereof. In further aspects, a LiPON material can comprise the structure $\text{Li}_{3+y}\text{PO}_{4-x}\text{N}_x$, where $y > 0$ and $0 < x < 4$. In further aspects, the solid-state electrolyte **108** can comprise lithium, lanthanum, zirconium, oxygen, or combinations thereof (e.g., each of lithium, lanthanum, zirconium, and oxygen – a LLZO compound). As used herein, “LLZO” refers to compounds including lithium, lanthanum, zirconium, and oxygen. In even further aspects, the solid-state electrolyte **108** can comprise a lithium-garnet, for example, at least one of: (i) $\text{Li}_{7-3a}\text{La}_3\text{Zr}_2\text{L}_a\text{O}_{12}$, with $\text{L} = \text{Al}, \text{Ga}$ or Fe and $0 < a < 0.33$; (ii) $\text{Li}_7\text{La}_{3-b}\text{Zr}_2\text{M}_b\text{O}_{12}$, with $\text{M} = \text{Bi}$ or Y and $0 < b < 1$; (iii) $\text{Li}_{7-c}\text{La}_3(\text{Zr}_2-$

$c, N_c)O_{12}$, with $N = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < c < 1$; (iv) protonated LLZO (e.g., $H_xLi_{6.5-x}La_3Zr_{1.5}I_{0.5}O_{12}$, with $I = \text{In, Si, Ge, Sn, V, W, Te, Nb, or Ta}$ and $0 < x < 4$ or $H_xLi_{6.25-x}E_{0.25}La_3Zr_2O_{12}$, with $E = \text{Al, Ga or Fe}$ and $0 < x < 4$), or a combination thereof. In aspects, the solid-state electrolyte **108** can comprise at least one of $Li_{10}GeP_2S_{12}$, $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, $Li_{1.4}Al_{0.4}Ti_{1.6}(PO_4)_3$, $Li_{0.55}La_{0.35}TiO_3$, interpenetrating polymer networks of poly(ethyl acrylate) (ipn-PEA) electrolyte, three-dimensional ceramic/polymer networks, in-situ plasticized polymers, composite polymers with well-aligned ceramic nanowires, PEO-based solid-state polymers, flexible polymers, polymeric ionic liquids, in-situ formed Li_3PS_4 , Li_6PS_5Cl , or combinations thereof.

[0107] As shown in **FIGS. 1-2**, the solid-state electrolyte **108** comprises the first major surface **109** and the second major surface **107** opposite the first major surface **109**, and a thickness (e.g., see thickness **707** in **FIG. 7**) of the solid-state electrolyte **108** can be defined between the first major surface **109** and the second major surface **107**. In aspects, the thickness of the solid-state electrolyte **108** can be about 20 μm or more, about 40 μm or more, about 60 μm or more, about 80 μm or more, about 100 μm or more, about 150 μm or more, about 300 μm or more, about 500 μm or more, about 600 μm or more, about 700 μm or more, about 800 μm or more, about 1 mm or more, about 2 mm or less, about 1.5 mm or less, about 1.2 mm or less, about 1 mm or less, about 800 μm or less, about 500 μm or less, about 300 μm or less, about 250 μm or less, about 200 μm or less, about 150 μm or less, about 120 μm or less, or about 100 μm or less. In aspects, the thickness of the solid-state electrolyte **108** can range from about 20 μm to about 2 mm, from about 40 μm to about 1.5 mm, from about 60 μm to about 1 mm, from about 80 μm to about 800 μm , from about 100 μm to about 500 μm , from about 150 μm to about 300 μm , from about 150 μm to about 250 μm , or any range or subrange therebetween. In aspects, the thickness of the solid-state electrolyte **108** can be about 300 μm or less, for example, from about 20 μm to about 300 μm , from about 40 μm to about 250 μm , from about 60 μm to about 200 μm , from about 80 μm to about 150 μm , from about 100 μm to about 150 μm , or any range or subrange therebetween. In aspects, the thickness of the solid-state electrolyte **108** can be about 500 μm or more, for example, from about 500 μm to about 2 mm, from about 600 μm to about 1.5 mm, from about 700 μm to about 1 mm, from about 800 μm to about 1 mm, or any range or subrange therebetween.

[0108] In aspects, the solid-state electrolyte **108** can comprise a sintered tape. As used herein, a sintered tape refers to a material formed by sintering a ceramic green-body comprising substantially the same thickness as the solid-state electrolyte. In further aspects, the solid-state electrolyte **108** comprising the sintered tape can comprise a thickness of about 300 μm or less, for

example, from about 20 μm to about 300 μm , from about 40 μm to about 250 μm , from about 60 μm to about 200 μm , from about 80 μm to about 150 μm , from about 100 μm to about 150 μm , or any range or subrange therebetween. In aspects, the solid-state electrolyte **108** can comprise consolidated pellets. As used herein, a solid-state electrolyte comprising consolidated pellets refers to a material that is formed by pressing together pellets that were previously sintered. As compared to a sintered tape, consolidated pellets can comprise larger grains and greater thickness. In further aspects, the solid-state electrolyte **108** comprising consolidated pellets can comprise a thickness of about 500 μm or more, for example, from about 500 μm to about 2 mm, from about 600 μm to about 1.5 mm, from about 700 μm to about 1 mm, from about 800 μm to about 1 mm, or any range or subrange therebetween.

[0109] As used herein, the surface profile is measured over a test area of 10 μm by 10 μm as measured using a confocal laser scanning microscope, which is used to characterize the major surfaces of the solid-state electrolyte using parameters defined in ISO 4287:1997. As used herein, surface roughness Ra is calculated as an arithmetical mean of the absolute deviation of a surface profile from an average position. As used herein, Ra is measured using a VK-X250 (Keyence) laser scanning microscope. In aspects, the first major surface **109** of the solid-state electrolyte **108** can comprise a surface roughness Ra of about 0.6 μm or less, about 0.5 μm or less, about 0.4 μm or less, about 0.05 μm or more, about 0.1 μm or more, about 0.2 μm or more, about 0.3 μm or more, or about 0.4 μm or more. In aspects, the first major surface **109** of the solid-state electrolyte **108** can comprise a surface roughness Ra in a range from about 0.05 μm to about 0.6 μm , from about 0.1 μm to about 0.5 μm , from about 0.2 μm to about 0.5 μm , from about 0.3 μm to about 0.5 μm , from about 0.4 μm to about 0.5 μm , or any range or subrange therebetween. Without wishing to be bound by theory, it is believed that the low roughness (e.g., about 0.6 μm or less or from about 0.1 μm to about 0.5 μm) of the first major surface enables increased charging rates by providing a substantially uniform surface for the anode, which enables uniform contact with the anode, reduces current concentration across the surface, and/or decreases the formation of dendrites.

[0110] In aspects, the second major surface **107** of the solid-state electrolyte **108** can comprise a surface roughness Ra of about 1 μm or more, about 1.2 μm or more, about 1.3 μm or more, about 1.4 μm or more, about 2.5 μm or less, about 3 μm or less, about 2.5 μm or less, about 2 μm or less, about 1.8 μm or less, about 1.6 μm or less, about 1.5 μm or less, or about 1.4 μm or more. In aspects, the second major surface **107** of the solid-state electrolyte **108** can comprise a surface roughness Ra in a range from about 1 μm to about 3 μm , from about 1 μm to about 2.5 μm , from about 1.2 μm to about 2 μm , from about 1.2 μm to about 1.8 μm , from about 1.3 μm to about

1.5 μm , from about 1.3 μm to about 1.4 μm , or any range or subrange therebetween. Without wishing to be bound by theory, it is believed that high roughness (e.g., about 1 μm or more or from about 1.2 μm to about 3 μm) of the second major surface decreases interfacial resistance by increasing a surface area of the interface between the solid-state electrolyte and the liquid electrolyte.

[0111] In aspects, the optional first coating **106** can comprise a carbon-based interlayer (e.g., interlinked freestanding, micro/mesopore containing, functionalized, biomass-derived), a polymer-based interlayer, a metal-based coating (e.g., Ni foam, etc.), a liquid electrolyte (e.g., LiPF_6 in ethylene carbonate (EC)/dimethyl carbonate (DMC)), ionic liquid-based (e.g., $\text{LiCF}_3\text{SO}_3/\text{CH}_3\text{CONH}_2$, LiTFSI/N -methylacetamide (NMA), $\text{PEO}_{18}\text{LiTFSI}$ -10% SiO_2 -10%IL, etc., where LiTFSI is bis(trifluoromethane) sulfonimide lithium salt ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$), SiO_2 may be nanoparticles, and IL is an ionic liquid), or a combination thereof. Exemplary aspects of polymer-based interlayers include carbon polysulfides (CS), polyethylene oxides (PEO), polyaniline (PANI), polypyrrole (PPY), poly(3,4-ethylenedioxythiophene) (PEDOT), poly(styrene sulfonic acid) (PSS), polyacrylonitrile (PAN), polyacrylic acid (PAA), polyallylamine hydrochloride (PAH), poly(vinylidene fluoride-co-hexafluoropropylene) (P(VDF-co-HFP)), poly(methyl methacrylate) (PMMA), polyvinylidene fluoride (PVDF), poly(diallyldimethyl ammonium) bis(trifluoromethanesulfonyl)imide (TFSI) (PDDATFSI), or combinations thereof. In aspects, the optional first coating **106** can comprise at least one of, or at least two of, or at least three elements selected from a group consisting of nitrogen, carbon, cobalt, titanium, tantalum, and tungsten.

[0112] In aspects, the optional second interlayer or coating **110** can comprise the materials or aspects discussed above the optional first coating **106** and/or the interlayer **114**. In aspects, the optional second interlayer or coating **110** can comprise an anode protector, for example, electrolyte additives (e.g., LiNO_3 , lanthanum nitrate, copper acetate, P_2S_5 , etc.), artificial interfacial layers (e.g., Li_3N , $(\text{CH}_3)_3\text{SiCl}$, Al_2O_3 , LiAl , etc.), composite metallics (e.g., Li_7B_6 , Li-rGO (reduced graphene oxide), layered Li-rGO, etc.), or combinations thereof. In aspects, the optional second interlayer or coating **110** can comprise a thin layer of metal (e.g., Au) that may be ion-sputter coated to form a contact interface between the anode **112** the solid-state electrolyte **108** and another material of the optional second interlayer or coating **110**. In aspects, the optional second interlayer or coating **110** can comprise a coating of lithium fluoride. In aspects, as shown in **FIG. 2**, the solid-state battery **201** may not have the optional second interlayer or second coating such that the anode **112** contacts the solid-state electrolyte **108**.

[0113] As shown in **FIGS. 1-2**, the anode **112** can be disposed on the solid-state electrolyte **108**. In aspects, as shown in **FIG. 2**, the first major surface **113** of the anode **112** can be disposed on the first major surface **109** of the solid-state electrolyte **108**. As shown, the anode **112** comprises a second major surface **115** opposite the first major surface **113** with an anode thickness **119** defined as an average distance therebetween when the solid-state battery **201** is in a fully charged state (defined below). In aspects, the anode thickness **119** can be about 1 micrometer (μm) or more, about 10 μm or more, about 50 μm or more, about 100 μm or more, about 150 μm or more, about 500 μm or less, about 400 μm or less, about 300 μm or less, or about 250 μm or less. In aspects, the anode thickness **119** can range from about 1 μm to about 500 μm , from about 10 μm to about 400 μm , from about 50 μm to about 300 μm , from about 100 μm to about 300 μm , from about 150 μm to about 250 μm , or any range or subrange therebetween.

[0114] The anode **112** is a lithium-containing anode. In aspects, the lithium-containing anode can consist essentially of lithium metal. Alternatively, in aspects, the lithium-containing anode can comprise an alloy of lithium and at least one of magnesium (Mg), silver (Ag), or combinations thereof. In further aspects, the lithium-containing alloy can further comprise a second component selected from a group consisting of calcium (Ca), aluminum (Al), gallium (Ga), boron (B), carbon (C), silicon (Si), tin (Sn), zinc (Zn), indium (In), antimony (Sb), silver (Ag), and combinations thereof. Exemplary aspects of the second component include calcium (Ca), tin (Sn), and silver (Ag). Providing a lithium-containing anode comprising a lithium alloy can increase a wettability of the anode on the coating, which can decrease interfacial resistance of the battery (e.g., by achieving and/or maintaining good contact with the solid-state electrolyte through the coating), facilitate a high area capacity of the battery, and/or facilitate a high charging current density of the battery.

[0115] **FIG. 2** illustrates a solid-state battery **201**. As shown in **FIG. 2**, the solid-state battery **201** can comprise a coin-cell form, although the battery can comprise another form in other aspects. Compared to **FIG. 1**, **FIG. 2** is a simplified solid-state battery **201** because the optional first coating **106** is omitted. Consequently, the interlayer **114** can be in direct contact with the cathode **104** and the solid-state electrolyte **108**, for example, because the optional first coating **106** is omitted. In aspects, as shown in **FIG. 2**, the area of the first major surface **113** of the anode **112** can be less than or equal to (e.g., less than) the area of the first major surface **109** of the solid-state electrolyte **108**. In further aspects, as shown, the area of the first major surface **113** of the anode **112** can be substantially equal to a corresponding area of the cathode **104**. Alternatively, as shown in **FIG. 1**, the area of the first major surface **113** of the anode **112** can be substantially equal to the

area of the first major surface **109** of the solid-state electrolyte **108**. In aspects, as shown in **FIG. 2**, an electrically insulating layer **205a and 205b** can be positioned between the first current collector **102** and the second current collector **116** to prevent a short circuit in the solid-state battery **201** and/or to form a barrier protecting the contents of the solid-state battery **201**. As used herein, the electrically insulating layer **205a and 205b** comprises an electronic conductivity of 10^{-5} S/cm or less. In even further aspects, as shown, the electrically insulating layer **205a and 205b** can be configured to maintain a configuration of the solid-state battery **201**, for example, by preventing the solid-state electrolyte **108** from contacting the second current collector **116**. In further aspects, the electrically insulating layer **205a and 205b** can comprise a polymeric material, for example, a fluoropolymer, a rubber, a polyurethane, or a silicone. In aspects, as shown, the solid-state battery **201** can further comprise an electrically conductive spacer **203** positioned between the anode **112** and the second current collector **116**. In further aspects, the electrically conductive spacer **203** can comprise a foam (e.g., Ni foam), which can help maintain contact between adjacent components of the solid-state battery and/or control an amount of stress that the components of the solid-state battery are subjected to. Although not shown, an electrically conductive spacer can be positioned between the cathode and the first current collector.

[0116] As used herein, “interfacial resistance” is measured using electrical impedance spectroscopy (EIS) at 25°C for frequencies from 0.1 Hertz (Hz) to 1 MegaHertz (MHz). Unless otherwise indicated, EIS was measured using a Solartron 1260A (Solartron) impedance analyzer. A Nyquist plot is constructed with the real component of impedance (Z' measured in $\Omega \text{ cm}^2$) on a horizontal axis and the imaginary component of impedance (Z'' measured in $\Omega \text{ cm}^2$) on a vertical axis. Throughout the disclosure, “interfacial resistance” is defined as the difference between the real components of the impedance for the end-points of an arc shape in EIS results (i.e., Nyquist plot), where the higher end-point is taken as an inflection point in the impedance results. For determining “interfacial resistance”, the battery is configured to be used with a lithium-containing anode disposed on the first major surface of the solid-state electrolyte and the second major surface of the solid-state electrolyte facing a cathode. In aspects, the interfacial resistance can be about $60 \Omega \text{ cm}^2$ or less, about $50 \Omega \text{ cm}^2$ or less, about $40 \Omega \text{ cm}^2$ or less, about $30 \Omega \text{ cm}^2$ or less, about $25 \Omega \text{ cm}^2$ or less, or about $20 \Omega \text{ cm}^2$ or less. In aspects, the interfacial resistance can range from about $10 \Omega \text{ cm}^2$ to about $60 \Omega \text{ cm}^2$, from about $10 \Omega \text{ cm}^2$ to about $50 \Omega \text{ cm}^2$, from about $10 \Omega \text{ cm}^2$ to about $40 \Omega \text{ cm}^2$, from about $15 \Omega \text{ cm}^2$ to about $30 \Omega \text{ cm}^2$, from about $20 \Omega \text{ cm}^2$ to about $25 \Omega \text{ cm}^2$, or any range or subrange therebetween. In aspects, the interfacial resistance of another battery, where the first major surface and the second major surface of the solid-state electrolyte are

switched, can be greater than the interfacial resistance of the battery where the major surfaces are not switched. In further aspects, the interfacial resistance of the battery (where the major surfaces are not switched), as a percentage of the another battery (where the major surfaces are switched), can be about 50% or less, about 40% or less, about 33% or less, or about 30% or less. In further aspects, the interfacial resistance of the battery (where the major surfaces are not switched), as a percentage of the another battery (where the major surfaces are switched), can range from about 5% to about 50%, from about 10% to about 40%, from about 20% to about 33%, from about 25% to about 30%, or any range or subrange therebetween.

[0117] Unless otherwise specified, a cycle comprises charging at 1C to a predetermined nominal areal capacity and discharged at 0.5C while the battery is maintained at 25°C. As used herein, “nominal capacity” (e.g., nominal areal capacity) refers to a capacity achieved using a predetermined charging condition in a first charging step for the battery. Areal capacity is presented based on a surface area of the anode. Unless otherwise indicated, battery testing including capacity retention and cycling at various nominal areal capacity is performed using the battery test system CT2001A (Landt) at 25°C. Unless otherwise indicated, the battery is configured with anode disposed on the first major surface of the solid-state electrolyte and the second major surface of the solid-state electrolyte facing the cathode. In aspects, the battery can withstand at least 10 cycles at a charging current density of 1.6 mA/cm² (1.6C) or more, about 1.8 mA/cm² (1.8C) or more, or about 2 mA/cm² (2C) to a nominal areal capacity of 1 mAh/cm² and a discharge current density of 0.5 mA/cm² (0.5C) at 25°C. As used herein, “withstand” indicates that the battery did not exhibit a short circuit or non-ohmic behavior during cycling. In aspects, another battery with the first major surface and the second major surface of the solid-state electrode swapped may not be able to withstand 10 cycles, 8 cycles, or 6 cycles at a charging current density of 1.25 mA/cm² (1.25C) to a nominal areal capacity of 1 mAh/cm² and a discharge current density of 0.5 mA/cm² (0.5C) at 25°C. In aspects, another battery with the first major surface and the second major surface of the solid-state electrode swapped may not be able to withstand 10 cycles at a charging current density of 1 mA/cm² (1C) or more, 1.25 mA/cm² (1.25C) or more, or 1.5 mA/cm² (1.5C) or more to a nominal areal capacity of 1 mAh/cm² and a discharge current density of 0.5 mA/cm² (0.5C) at 25°C. In aspects, after 60 cycles or more (e.g., charging at 1C to a nominal areal capacity of 1 mAh/cm² and discharging at 0.5C at 25°C) with a cutoff voltage of 4.5V, the battery can exhibit a capacity retention of 90% or more, 92% or more, or 95% or more. In aspects, after 60 cycles or more (e.g., charging at 1C to a nominal areal capacity of 1 mAh/cm² and discharging at 0.5C) at 60°C with a cutoff voltage of 4.5V, the battery can exhibit a capacity retention of 90% or more,

92% or more, or 95% or more. In aspects, after 60 cycles or more with cycles comprising charging at 0.5C to a nominal areal capacity of 3 mAh/cm² and discharging at 0.17C at 60°C with a cutoff voltage of 4.5V, the battery can exhibit a capacity retention of 90% or more, 92% or more, or 95% or more.

[0118] Aspects of methods of treating the solid-state electrolyte and/or methods of making the solid-state battery in accordance with aspects of the disclosure will be discussed with reference to example method steps illustrated in **FIGS. 3-10**. Methods can comprise providing a solid-state electrolyte, which can comprise one or more of the materials discussed above with reference to the solid-state electrolyte. In aspects, the solid-state electrolyte can comprise a sintered tape, for example, with a thickness from about 20 μm to about 300 μm. Alternatively, in aspects, the solid-state electrolyte can comprise consolidated pellets, for example, with a thickness from about 500 μm to about 2 mm.

[0119] In aspects, as shown in **FIGS. 7 and 9**, methods comprise polishing an initial first major surface of the solid-state electrolyte **108** to obtain a predetermined first surface roughness Ra of the first major surface **109**. The predetermined first surface roughness can be within one or more of the ranges discussed above for the surface roughness Ra of the first major surface of the solid-state electrolyte, for example, about 0.6 μm or less or from about 0.1 μm to about 0.5 μm. In further aspects, a thickness **707** of the solid-state electrolyte **108** (e.g., between the first major surface **109** and an initial second major surface **705**) before the polishing can be substantially identical to the thickness of the solid-state electrolyte in the solid-state battery **101 or 201**.

[0120] In further aspects, as shown in **FIG. 7**, the polishing the first major surface **109** can comprise etching the first major surface **109** with an acidic solution **703**. In even further aspects, as shown, the acidic solution **703** can be contained in an acidic bath **701**. In even further aspects, as shown, the first major surface **109** can be etched without simultaneously etching the second major surface **107**, although the major surfaces may be etched simultaneously for at least a portion of the time in other aspects. In even further aspects, the acidic solution can comprise a mineral acid (e.g., HCl, HNO₃, H₂SO₄, H₃PO₄). In still further aspects, a concentration of the mineral acid can be about 0.1 molar (M) or more, about 0.5 M or more, about 1 M or more, about 1.5 M or more, about 3 M or less, about 2 M or less, or about 1.5 M or less. In still further aspects, a concentration of the mineral acid can range from about 0.1 M to about 3 M, from about 0.5 M to about 2 M, from about 1 M to about 1.5 M, or any range or subrange therebetween. In even further aspects, the acidic solution can comprise a pH of about 3 or less, about 1 or less, or about 1 or less. In further aspects, the acidic solution can be maintained at a temperature of about 20°C or more,

about 25°C or more, about 30°C or more, about 40°C or less, about 35°C or less, or about 30°C or less. In further aspects, the acidic solution can be maintained at a temperature in a range from about 20°C to about 40°C, from about 20°C to about 35°C, from about 25°C to about 30°C, or any range or subrange therebetween. In further aspects, the etching (e.g., contact between the acidic solution and the first major surface) can occur for about 4 minutes or less, about 3 minutes or less, about 2 minutes or less, about 10 seconds or more, about 30 seconds or more, or about 1 minute or more. In further aspects, the etching can occur for from about 10 seconds to about 4 minutes, from about 30 seconds to about 3 minutes, from about 1 minute to about 2 minutes, or any range or subrange therebetween. Without wishing to be bound by theory, etching for a short period of time (e.g., about 4 minutes or less) can reduce surface irregularities without increasing a surface roughness of the first major surface (e.g., by etching grain boundaries of the solid-state electrolytes).

[0121] Alternatively, in further aspects, as shown in **FIG. 9**, the polishing the first major surface **109** can comprise mechanical polishing. For example, as shown, mechanically polishing the first major surface **109** can comprise rotating (as indicated by arrow **903**) a grinding tool **901** comprising a grinding surface **907** of an abrasive **905**. In even further aspects, the abrasive **905** of the grinding surface **907** can comprise a grit of about 1000 or more (e.g., median particle size of about 10 micrometers or less) or about 1200 or more (e.g., median particle size of about 8 micrometers or less). In even further aspects, the abrasive **905** can comprise a greater hardness than the solid-state electrolyte **108**, for example, the abrasive can comprise silicon carbide or another material used in “sandpaper.” Providing a high grit (or low median particle size) abrasive for mechanically polishing the first major surface can produce a low surface roughness of the first major surface.

[0122] In aspects, as shown in **FIGS. 8 and 10**, methods can further comprise polishing an initial second major surface **705** of the solid-state electrolyte **108** to obtain a predetermined second surface roughness R_a of the second major surface **107**. The predetermined second surface roughness can be within one or more of the ranges discussed above for the surface roughness R_a of the second major surface of the solid-state electrolyte, for example, about 1 μm or more or from about 1.2 μm to about 3 μm .

[0123] In further aspects, as shown in **FIG. 8**, the polishing the initial second major surface **705** (see **FIGS. 7 and 9**) to form the second major surface **107** can comprise etching the second major surface **107** or **705** with an acidic solution **803**. In even further aspects, as shown, the acidic solution **803** can be contained in an acidic bath **801**. In even further aspects, the acidic solution **803** can comprise a mineral acid (e.g., HCl, HNO₃, H₂SO₄, H₃PO₄). In still further aspects,

a concentration of the mineral acid can be about 0.1 molar (M) or more, about 0.5 M or more, about 1 M or more, about 1.5 M or more, about 3 M or less, about 2 M or less, or about 1.5 M or less. In still further aspects, a concentration of the mineral acid can range from about 0.1 M to about 3 M, from about 0.5 M to about 2 M, from about 1 M to about 1.5 M, or any range or subrange therebetween. In even further aspects, the acidic solution can comprise a pH of about 3 or less, about 1 or less, or about 1 or less. In further aspects, the acidic solution can be maintained at a temperature of about 20°C or more, about 25°C or more, about 30°C or more, about 40°C or less, about 35°C or less, or about 30°C or less. In further aspects, the acidic solution can be maintained at a temperature in a range from about 20°C to about 40°C, from about 20°C to about 35°C, from about 25°C to about 30°C, or any range or subrange therebetween. In even further aspects, as shown, the second major surface **107 or 705** can be etched without simultaneously etching the first major surface **109**, although the major surfaces may be etched simultaneously for at least a portion of the time that the second major surface is etched. In further aspects, the etching (e.g., contact between the acidic solution and the second major surface) can occur for about 7 minutes or more, about 10 minutes or more, about 15 minutes or more, about 30 minutes or less, about 25 minutes or less, about 20 minutes or less, or about 15 minutes or less. In further aspects, the etching can occur for from about 7 minutes to about 30 minutes, from about 7 minutes to about 25 minutes, from about 7 minutes to about 20 minutes, from about 10 minutes or about 15 minutes, or any range or subrange therebetween. In even further aspects, the polishing the first major surface (see **FIG. 7**) and the second major surface (see **FIG. 8**) can both comprise etching the corresponding major surface. In still further aspects, the period of time that the second major surface is etched can be greater than the period of time that the first major surface is etched, for example, by about 3 minutes or more, about 5 minutes or more, or about 7 minutes or more. It is to be understood that the first major surface can be polished by etching and/or mechanical polishing in conjunction with etching the second major surface. Without wishing to be bound by theory, etching for a longer period of time (e.g., about 7 minutes or more) can increase a surface roughness of the second major surface, for example by etching grain boundaries of the solid-state electrolytes and/or leaching portions of the solid-state electrolyte.

[0124] Alternatively, in further aspects, as shown in **FIG. 10**, the polishing the initial second major surface **705** (see **FIGS. 7 and 9**) to form the second major surface **107** can comprise mechanical polishing. For example, as shown, mechanically polishing the second major surface **107 or 705** can comprise rotating (as indicated by arrow **1003**) a grinding tool **1001** comprising a grinding surface **1007** of an abrasive **1005**. In even further aspects, the abrasive **1005** of the

grinding surface **1007** can comprise a grit of about 600 or less (e.g., median particle size of about 20 micrometers or more) or about 400 or less (e.g., median particle size of about 25 micrometers or more). In even further aspects, the abrasive **1005** can comprise a greater hardness than the solid-state electrolyte **108**, for example, the abrasive can comprise silicon carbide or another material used in “sandpaper.” In even further aspects, the polishing the first major surface (see **FIG. 9**) and the second major surface (see **FIG. 10**) can both comprising mechanically polishing the corresponding major surface. In still further aspects, a grit of the abrasive used to mechanically polish the first major surface can be greater than a grit of the abrasive used to mechanically polish the second major surface by about 200 or more, about 400 or more, or about 600 or more. In still further aspects, a median particle size of the abrasive used to mechanically polish the first major surface can be less than a median particle size of the abrasive used to mechanically polish the second major surface, for example, by about 5 μm or more, about 10 μm or more, or about 12 μm or more. It is to be understood that the first major surface can be polished by etching or mechanical polishing in conjunction with mechanically polishing the second major surface. Providing a low grit (or high median particle size) abrasive for mechanically polishing the second major surface can produce a high surface roughness of the second major surface. Methods of treating the solid-state electrolyte can be complete after polishing the first major surface and polishing the second major surface.

[0125] Methods of making a battery (e.g., solid-state battery) can further comprise disposing an anode on the first major surface of the solid-state electrolyte. In aspects, as shown in **FIG. 3**, methods can comprise disposing a lithium-containing material **305** on the first major surface **109** of the solid-state electrolyte **108**. In further aspects, as shown, disposing the lithium-containing material **305** can comprise dispensing one or more molten metals **303** (e.g., elemental metal or alloy in the molten state) from a source **301** (e.g., metal foil, conduit, micropipette, or syringe). Alternatively, disposing the lithium-containing material **305** for the anode **112** can comprise deposition from a gas phase, for example, by sputtering from one or more sources (e.g., elemental targets or an alloy target) and/or by thermal evaporation, although other methods of physical vapor deposition (PVD) can be used to form the anode **112**. In aspects, the lithium-containing material **305** and/or anode **112** can consist essentially of lithium metal. Alternatively, in aspects, the lithium-containing material **305** and/or anode **112** can comprise an alloy of lithium with one or more of magnesium, silver, or combinations thereof. Alternatively, the lithium-containing material can be disposed on the solid-state electrolyte by attaching a metal foil

comprising the lithium-containing material to the first major surface of the solid-state electrolyte, which can be treated as discussed below with reference to **FIG. 4**.

[0126] In aspects, after or during disposing the alloy (e.g., lithium-containing material **305**, anode **112**), as shown in **FIG. 4**, the solid-state electrolyte **108** and the lithium-containing material (e.g., anode **112**) can be in an environment maintained at a first temperature. For example, as shown, the solid-state electrolyte **108** can be placed in an oven **401** maintained at the first temperature. The first temperature is greater than a melting point of the one or more materials used to form the anode. In further aspects, the first temperature can be greater than a melting point of the one or more materials used to form the anode by about 50°C or more, about 100°C or more, about 125°C or more, or about 150°C or more. For example, lithium metal has a melting temperature of about 180°C. In aspects, the first temperature can be about 280°C or more, about 300°C or more, about 320°C or more, about 500°C or less, about 400°C or less, or about 350°C or less, for example, from about 280°C to about 500°C, from about 300°C to about 400°C, from about 320°C to about 350°C, or any range or subrange therebetween. In further aspects, after disposing the lithium-containing material, the solid-state electrolyte **108** and the lithium-containing material can be maintained at the first temperature for about 1 minute or more, about 3 minutes or more, about 5 minutes or more, about 15 minutes or more, about 20 minutes or more, about 1 hour or less, about 45 minutes or less, about 30 minutes or less, or about 25 minutes or less. In further aspects, after disposing the lithium-containing material, the solid-state electrolyte **108** and the lithium-containing material can be maintained at the first temperature for a time ranging from about 1 minute to about 1 hour, from about 3 minutes to about 45 minutes, from about 5 minutes to about 30 minutes, from about 15 minutes to about 30 minutes, from about 20 minutes to about 25 minutes, or any range or subrange therebetween. Providing a temperature and time within one or more of the above-mentioned ranges can enable the lithium-containing material to wet or otherwise conform to the first major surface **109** of the solid-state electrolyte **108**. As discussed in the Examples, an anode consisting essentially of lithium may be heated at about 330°C or more (e.g., from about 330°C to about 400°C) to ensure that the resulting anode forms intimate and/or uniform contact with the first major surface of the solid-state electrolyte while lithium alloys may be heated at a broader range of temperatures (e.g., about 300°C or more) to achieve similar properties and/or performance.

[0127] In aspects, as shown in **FIG. 5**, methods can further comprise disposing an interlayer **114** by disposing a liquid electrolyte **505** on the cathode **104**. In further aspects, the liquid electrolyte can comprise a lithium salt and a solvent, which can comprise one or more of the

materials discussed above for the interlayer **114**. In further aspects, a concentration of the lithium salt in the solvent can be within one or more of the corresponding ranges discussed above. In further aspects, as shown, disposing the liquid electrolyte **505** can comprise dispensing a predetermined amount of the liquid **503** from a container **501** (e.g., conduit, flexible tube, micropipette, or syringe) to form the liquid electrolyte **505** on a first major surface **105** of the cathode **104**. In further aspects, the predetermined amount of the interlayer **114** (e.g., liquid electrolyte **505**) as a ratio of a volume of the interlayer (e.g., liquid electrolyte) to an area of the first major surface of the cathode can be within one or more of the corresponding ranges discussed above. Providing the ratio of the volume of the interlayer to the area of the first major surface of the cathode can be sufficient to wet the interface between the cathode and the solid-state electrolyte while minimizing concerns associated with traditional liquid electrolytes (e.g., in liquid-based batteries or in hybrid liquid-solid batteries). Although not shown, the cathode can be disposed on the first current collector while the interlayer is disposed on the cathode.

[0128] In aspects, as shown in **FIG. 6**, method can further comprise disposing the solid-state electrolyte **108** on the cathode **104**, as indicated by arrow **601**. As shown, the cathode **104** can be opposite the first major surface **109** of the solid-state electrolyte **108**, the optional second interlayer or coating **110**, and/or the anode **112**. As shown, the solid-state electrolyte **108** is positioned between the cathode **104** and the anode **112**. Although not shown, additional elements (e.g., current collectors) can be present when the solid-state electrolyte is disposed on the cathode and/or additional elements can be added after disposing the cathode to form the battery (e.g., solid-state battery **101** or **201**).

EXAMPLES

[0129] Various aspects will be further clarified by the following examples. Examples A-D are lithium garnet (discussed below) solid-state electrolytes polished under different conditions. Examples C-D, Example 1, and Comparative Examples (CE) AA-CC comprised sintered tapes of the lithium garnet (discussed below) solid-state electrolyte comprising a thickness of 120 μm and a diameter of 14 mm. Examples A-B, Examples 2 and 4, and Comparative Examples DD-FF and II-KK comprised consolidated pellets of the lithium garnet (discussed below) solid-state electrolyte with a net thickness of 600 μm and diameter of 14 mm. Example 3 and Comparative Examples GG-HH comprised the sintered tapes of the lithium garnet (discussed below) solid-state electrolyte comprising a thickness of 120 μm , a width of 25.4 mm, and a length of 25.4 mm (1 inch square).

[0130] Example 1 and Comparative Examples AA—cc comprised a lithium cobaltite (LCO) cathode with a mass loading of 20 mg/cm^2 of the cathode and a diameter of 12 mm.

Examples 2 and 4 and Comparative Examples AA—FF and II-KK comprised a NCM523 cathode with a mass loading of 20 mg/cm² of the cathode and a diameter of 12 mm. Example 3 comprised the NCM 523 cathode with the mass loading of 20 mg/cm², a width of 20 mm, and a length of 20 mm. For Examples 1-3 and Comparative Examples AA-HH, the anode comprises a lithium alloy of 10 atom% magnesium with the balance as lithium metal. For Example 4 and Comparative Examples II-KK, the anode consisted of lithium metal.

[0131] NCM523 refers to LiNi_{0.5}Co_{0.2}Mn_{0.3}O₂ (precursor commercially available from Landt Instruments). The NCM523 and LCO, respectively, were formed into slurry with a 8:1:1 weight ratio of the precursor, super P carbon black (available from Timcal – Imerys), and poly(vinylidene fluoride) (PVDF) (dissolved in N-methylpyrrolidone) that was coated on aluminum (Al) foil with a predetermined thickness and dried under vacuum. After polishing the surfaces of the solid-state electrolyte (discussed below and in Tables 1-4), the lithium-containing material for the anode was disposed on the coating and heated for 5 minutes at 300°C (Examples 1-3 and Comparative Examples AA-HH and JJ-KK) or at 330°C (Example 4 and Comparative Example II). In Examples 1-4 and Comparative Examples AA-KK, 10 μL/cm² of a liquid electrolyte comprising 1.2 M LIFSI dissolved in sulfolane was disposed on the cathode, and then the solid-state electrolyte was disposed over the cathode with the liquid electrolyte positioned therebetween. Examples 1-2 and 4 and Comparative Examples AA-FF and II-KK were formed into a battery resembling the solid-state battery **201** shown in **FIG. 2** in a CR2025 coin cell form with Ni foam disposed over the anode. Examples 3 and Comparative Examples GG-HH were formed into a pouch cell using an aluminum-plastic film.

[0132] The lithium garnet solid-state electrolyte was cubic phase Li_{6.5}La₃Zr_{1.4}Ta_{0.5}O₁₂ (LLZTO), which was synthesized from a stoichiometric ratio of starting powders of LiOH•H₂O (AR), La₂O₃ (99.99%), ZrO₂ (AR), Ta₂O₅ (99.99%). 2 wt% excess of LiOH•H₂O added to compensate the lithium loss during processing. La₂O₃ was heated at 900°C for 12 hours to remove any moisture and/or CO₂. The raw materials were mixed via a wet grinding process in which yttrium-stabilized zirconium oxide (YSZ) balls and isopropanol (IPA) were used as the milling media. For the consolidated pellets, the pellets were formed by drying and calcining the mixture at 950°C for 6 hours in an alumina crucible, producing pure cubic garnet phase powder. These powders were pressed into green pellets and sintered at 1230°C for 1 hour, covered with LLZTO powder with 15 wt% Li excess in platinum crucibles. For the sintered tape, the mixture was mixed with an organic binder system comprising a propionate solvent, a dispersant, a plasticizer, and an

acrylate-based polymer, which was tape cast with a doctor blade to form a green tape. The green tape was sintered at from 1000°C to 1300°C for 10 minutes.

[0133] As shown in Table 1, a surface of the lithium garnet solid-state electrolyte was treated with a 1M HCl solution at 25°C or mechanical polishing with a silicon carbide (SiC) abrasive. for Examples A-D. Unless otherwise indicated with reference to the Examples and Comparative Examples, “etch” means treatment with a 1M HCl solution at 25°C, and “SiC” means mechanical polishing with an SiC abrasive. **FIG.11(a)-(d)** schematically represent scanning electron microscope (SEM) images for Examples A-D at the same scale (magnification) with the contrast enhanced to improve visibility. As shown in **FIG. 11(a)**, Example A with the surface etched for 1 minute has a flat surface with smooth grain boundaries visible defining the garnet grains of the consolidated pellets **1101**. As shown in **FIG. 11(b)**, Example B with the surface etched for 10 minutes is porous with pores **1105** formed between the grains **1103** that have been etched to have an irregular appearance. As shown in Table 1, the surface roughness Ra of Example A was 0.5 µm while it was 1.5 µm for Example B. Consequently, increased etching times are associated with increased surface roughness. Without wishing to be bound by theory, it is believed that relatively short etching times can reduce surface irregularities without increasing a surface roughness of the first major surface (e.g., by etching grain boundaries of the solid-state electrolytes) while relatively long etching times can increase a surface roughness of the first major surface for example by etching grain boundaries of the solid-state electrolytes and/or leaching portions of the solid-state electrolyte. As shown in **FIG. 11(c)**, Example C with the surface mechanically polished with a 1200 grit SiC abrasive (median particle size of about 8 µm) was smooth and flat with small flaws **1111** associated with the abrasive grain and no discernable texture of the grains in the sintered tape. As shown in **FIG. 11(d)**, Example D with the surface mechanically polished with a 400 grit SiC abrasive (median particle size of about 25 µm) was coarse with visible grains **1115** in the sintered tape and several large scratches **1113** associated with the abrasive grain. As shown in Table 1, the surface roughness Ra of Example C was 0.4 µm while it was 1.2 µm for Example D. Consequently, increasing grit (decreasing particle size) is associated with decreased surface roughness. For Examples 1-4 and Comparative Examples AA-KK, the treatments for each major surface were chosen from the treatments in Examples A-D, with the method (etching versus SiC) and the resulting surface roughness Ra indicated in Tables 2-4.

Table 1: Properties of Examples A-D

Example	Treatment	Surface Roughness	Appearance
A	Etch: 1 minute 1M HCl, 25°C	0.5 μm	FIG. 11(a) Flat surface, smooth grains
B	Etch: 10 minutes 1M HCl, 25°C	1.5 μm	FIG. 11(b) Porous, irregular grains
C	1200 grit SiC	0.4 μm	FIG. 11(c) Smooth and flat, small flaws
D	400 grit SiC	1.2 μm	FIG. 11(d) Very coarse with scratches

[0134] Table 2 presents the properties for Examples 1-2 and Comparative Examples AA-FF. As mentioned above, Example 1 and Comparative Examples AA-CC comprised a sintered tape solid-state electrolyte that was etched to achieve the roughness values shown in Table 2; and Example 2 and Comparative Examples DD-FF comprised a consolidated pellet solid-state electrolyte that were mechanically polished to achieve the roughness values shown in Table 2. Examples 1-2 comprised a surface roughness Ra of the first major surface 0.6 μm or less that was less than the surface roughness Ra of the second major surface that was greater than 1 μm . Comparative Examples BB and EE are the same as Examples 1 and 2, respectively, with the surface roughness Ra of the first major surface and the second major surface switched. Both major surfaces in Comparative Examples AA and DD comprised a surface roughness Ra 0.6 μm or less, and both major surfaces in Comparative Examples CC and FF comprised a surface roughness Ra greater than 1 μm .

Table 2: Properties of Examples 1-2 and Comparative Examples AA-FF

Example	Solid-state electrolyte	Anode-side roughness (1 st Major Surface)	Cathode-side roughness (2 nd Major Surface)	Interfacial Resistance ($\Omega\text{ cm}^2$)	Maximum charging current density (mA/cm^2)
1	Sintered Tape	Etch: 0.5 μm	Etch: 1.5 μm	20	2*
CE AA	Sintered Tape	Etch: 0.5 μm	Etch: 0.5 μm	80	2*
CE BB	Sintered Tape	Etch: 1.5 μm	Etch: 0.5 μm	75	1.25
CE CC	Sintered Tape	Etch: 1.5 μm	Etch: 1.5 μm	20	1.5

2	Consolidated Pellets	SiC: 0.4 μm	SiC: 1.2 μm	60	0.8
CE DD	Consolidated Pellets	SiC: 0.4 μm	SiC: 0.4 μm	120	0.8*
CE EE	Consolidated Pellets	SiC: 1.2 μm	SiC: 0.4 μm	110	0.6
CE FF	Consolidated Pellets	SiC: 1.2 μm	SiC: 1.2 μm	60	0.6

* = example withstood all charging current densities tested

[0135] **FIG. 12** shows a Nyquist plot for Example 1 and Comparative Examples AA-CC; and **FIG. 13** shows a Nyquist plot for Example 2 and Comparative Examples DD-FF. As discussed above, the data shown in **FIGS. 12-13** were measured by EIS using Solartron 1260A (Solartron) impedance analyzer at 25°C for frequencies from 0.1 Hertz (Hz) to 1 MegaHertz (MHz). In **FIGS. 12-13**, the horizontal axis **1201 and 1301** corresponds to the real component of impedance (Z' measured in $\Omega \text{ cm}^2$), and the vertical axis **1203 and 1303** corresponds to the imaginary component of impedance (Z'' measured in $\Omega \text{ cm}^2$). As discussed above, the interfacial resistance shown in Table 2 is measured as the difference between the real components of the impedance for the end-points of an arc shape of the curve corresponding to the EIS results in the Nyquist plot. Curves **1207 and 1209** correspond to Comparative Examples AA and BB, respectively, with an interfacial resistance greater than 70 $\Omega \text{ cm}^2$. Curves **1205 and 1211** correspond to Example 1 and Comparative Example CC, respectively, with an interfacial resistance of about 20 $\Omega \text{ cm}^2$. Consequently, the lower surface roughness Ra (e.g., 0.6 μm or less) of the first major surface in Example 1 and Comparative Example CC produce a lower surface roughness than the higher surface roughness Ra (e.g., greater than 1 μm) of the first major surface in Comparative Examples AA-BB. Similarly, Curves **1307 and 1309** correspond to Comparative Examples DD and EE, respectively, with an interfacial resistance of 110 $\Omega \text{ cm}^2$ or more while curves **1305 and 1311** correspond to Example 2 and Comparative Example FF, respectively, with an interfacial resistance of about 60 $\Omega \text{ cm}^2$ or less. Therefore, Examples 1-2 achieve an interfacial resistance of about 60 $\Omega \text{ cm}^2$ or less. While the interfacial resistance is lower for the sintered tape (Example 1) relative to the consolidated tape (Example 2), the trend of the lower surface roughness Ra (e.g., 0.6 μm or less) of the first major surface being associated with decreased interfacial resistance is consistent across **FIGS. 12-13**.

[0136] **FIGS. 14-17** show capacity-voltage (CV) curves for Comparative Example AA, Example 1, and Comparative Examples BB-CC, respectively. For **FIGS. 14-17**, the batteries were

tested at a nominal areal capacity of 1 mAh/cm² with a discharging rate of 0.5C at 25°C for all cycles whereas the charging current density (or charging rate) varied. Initially, the charging current density was 0.5 mA/cm² (0.5C) and increased by 0.25 mA/cm² (0.25 C) every 10 cycles to a maximum of 2 mA/cm² (2C) with the last cycle at a given charging current density (until failure) shown in **FIGS. 14-17** for simplicity. In **FIGS. 14-17**, the horizontal axis **1401** corresponds to the instantaneous capacity in mAh/cm², and the vertical axis **1403** corresponds to voltage in volts (V). In **FIG. 14**, curves **1405, 1407, 1409, 1411, 1413, 1415, and 1417** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.5C, 0.75C, 1C, 1.25C, 1.5C, 1.75C, and 2C, respectively. Curves **1421** correspond to the charging curves from 0.5C to 2C that superimpose on one another. All of the charging curves in **FIG. 14** (up to 2C) appear normal. In **FIG. 15**, curves **1505, 1507, 1509, 1511, 1513, 1515, and 1517** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.5C, 0.75C, 1C, 1.25C, 1.5C, 1.75C, and 2C, respectively. Curves **1521** correspond to the charging curves from 0.5C to 2C that superimpose on one another. All of the charging curves in **FIG. 15** (up to 2C) appear normal. Therefore, Example 1 and Comparative Example AA can withstand at least 10 cycles to a nominal areal capacity of 1 mAh/cm² with a charging rate of 2C and a discharging rate of 0.5C at 25°C.

[0137] FIGS. 16-17 show capacity-voltage (CV) curves for Comparative Examples BB-CC, respectively. In **FIG. 16**, curves **1605, 1607, 1609, and 1611** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.5C, 0.75C, 1C, and 1.25C, respectively. Curves **1621** correspond to the charging curves at 0.5C, 0.75C, and 1C that superimpose on one another while curve **1623** corresponds to the charging curve at 1.25C. Curve **1611** shows irregularities (e.g., non-ohmic behavior), and curve **1623** indicates that there was a short circuit at 1.25C. In **FIG. 17**, curves **1705, 1707, 1709, 1711, and 1713** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.5C, 0.75C, 1C, 1.25C, and 1.5C, respectively. Curves **1721** correspond to the charging curves 0.5C, 0.75C, and 1C that superimpose on one another. Curve **1723** corresponds to charging at 1.25C, and curve **1725** corresponds to charging at 1.5C. Curve **1713** shows irregularities, curve **1723** indicates reduced capacity when charging at 1.25C, and curve **1725** indicates failure when charging at 1.5C. Therefore, Comparative Examples BB-CC are unable to withstand charging at 1.5C (or 1.25C) to a nominal areal capacity of 1 mAh/cm² at 25°C for at least 10 cycles without irregularities or failure. Comparing, Example 1 and Comparative Example AA with Comparative Examples BB-CC, the surface roughness Ra of the second major surface is the distinguishing characteristic. Based on the results in **FIGS. 14-17**, providing a surface roughness Ra of the second major surface of 1 μm or more (e.g., 1.4 μm, 1.5 μm) increases the

charging current density that the battery can withstand (e.g., relative to a surface roughness of 0.6 μm or less).

[0138] **FIGS. 18-21** show capacity-voltage (CV) curves for Comparative Example DD, Example 2, and Comparative Examples EE-FF, respectively. For **FIGS. 18-21**, the batteries were tested at a nominal areal capacity of 1 mAh/cm² with a discharging rate of 0.5C at 25°C for all cycles whereas the charging current density (or charging rate) varied. Unlike Example 1 and Comparative Examples AA-CC with the sintered tape, for Example 2 and Comparative Examples DD-FF with the consolidated pellets, the charging current density was initially 0.4 mA/cm² (0.4C) and increased by 0.2 mA/cm² (0.2 C) every 10 cycles to a maximum of 0.8 mA/cm² (0.8C) with the last cycle at a given charging current density (until failure) shown in **FIGS. 18-21** for simplicity. In **FIGS. 18-21**, the horizontal axis **1801** corresponds to the instantaneous capacity in mAh/cm², and the vertical axis **1803** corresponds to voltage in volts (V). In **FIG. 18**, curves **1805**, **1807**, and **1809** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C, 0.6C, and 0.8C, respectively. Curves **1811**, **1813**, and **1815** correspond to the charging curves at 0.4C, 0.6C, and 0.8C, respectively. All of the charging curves in **FIG. 18** (up to 0.8C) appear normal even though the charging curves do not exactly superimpose on one another. In **FIG. 19**, curves **1905**, **1907**, and **1909** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C, 0.6C, and 0.8C, respectively. Curves **1911**, **1913**, and **1915** correspond to the charging curves at 0.4C, 0.6, and 0.8C, respectively. All of the discharging curves in **FIG. 19** (up to 0.8C) appear normal. However, curve **1915** indicates that there was a short circuit when charging at 0.8C. Therefore, Example 2 and Comparative Example DD can withstand at least 10 cycles to a nominal areal capacity of 1 mAh/cm² with a charging rate of 0.6C or more (e.g., 0.8C) and a discharging rate of 0.5C at 25°C when the second major surface has a high surface roughness Ra (e.g., about 1 μm or more).

[0139] **FIGS. 20-21** show capacity-voltage (CV) curves for Comparative Examples EE-FF, respectively. In **FIG. 20**, curves **2005** and **2007** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C and 0.6C, respectively. Curves **2011** and **2013** correspond to the charging curves at 0.4C and 0.6C, respectively. Curve **2013** indicates that there was a short circuit at 0.6C. In **FIG. 21**, curves **2105** and **2107** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C and 0.6C, respectively. Curves **2111** and **2113** correspond to the charging curves 0.4C and 0.6C, respectively. Curve **2113** indicates failure when charging at 0.6C. Therefore, Comparative Examples EE-FF are unable to withstand charging at 0.6C to a nominal areal capacity of 1 mAh/cm² at 25°C for at least 10 cycles without failure (e.g., short

circuit). Comparing, Example 2 and Comparative Example DD with Comparative Examples EE-FF, the surface roughness Ra of the second major surface is the distinguishing characteristic. Based on the results in **FIGS. 18-21**, providing a surface roughness Ra of the second major surface of 1 μm or more (e.g., 1.4 μm , 1.5 μm) increases the charging current density that the battery can withstand (e.g., relative to a surface roughness of 0.6 μm or less).

[0140] For Example 3 and Comparative Examples GG-HH comprised pouch cell batteries with the properties shown in Table 3. **FIG. 22** shows a Nyquist plot for Example 3 and Comparative Examples GG-HH. In **FIG. 22**, the horizontal axis **2201** corresponds to the real component of impedance (Z' measured in $\Omega \text{ cm}^2$), and the vertical axis **2203** corresponds to the imaginary component of impedance (Z'' measured in $\Omega \text{ cm}^2$). As discussed above, the interfacial resistance shown in Table 3 is measured as the difference between the real components of the impedance for the end-points of an arc shape of the curve corresponding to the EIS results in the Nyquist plot. Curves **2205**, **2207**, and **2209** correspond to Example 3 and Comparative Examples GG-HH, respectively. Example 3 and Comparative Example HH comprised an interfacial resistance of 20 $\Omega \text{ cm}^2$ or less (e.g., 15 $\Omega \text{ cm}^2$ or less, 10 $\Omega \text{ cm}^2$ or less). Comparative Example GG has an interfacial resistance greater than 60 $\Omega \text{ cm}^2$ (e.g., 70 $\Omega \text{ cm}^2$ or less). Consequently, the lower surface roughness Ra (e.g., 0.6 μm or less) of the first major surface in Example 3 and Comparative Example HH produce a lower surface roughness than the higher surface roughness Ra (e.g., greater than 1 μm) of the first major surface in Comparative Example GG.

Table 3: Properties of Example 3 and Comparative Examples GG-HH pouch cells

Example	Anode-side roughness (1 st Major Surface)	Cathode-side roughness (2 nd Major Surface)	Interfacial Resistance ($\Omega \text{ cm}^2$)	Cycles Withstood (Capacity: 3 mAh/cm ² ; 0.5C charge/discharge; 60°C)
3	Etch: 0.5 μm	Etch: 1.5 μm	15	60*
CE GG	Etch: 0.5 μm	Etch: 0.5 μm	70	< 20
CE HH	Etch: 1.5 μm	Etch: 1.5 μm	10	< 20

* = example withstood all cycles tested

[0141] **FIG. 23** shows the capacity performance of Example 3 and Comparative Examples GG-HH when cycles to a nominal capacity of 3 mAh/cm² with a charging rate of 0.5C (1.5 mAh/cm²) and a discharging rate of 0.17C (0.5 mAh/cm²) at 60°C. In **FIG. 23**, horizontal axis **2301** represents the cycle number, and vertical axis **2303** corresponds to the actual capacity at the

end of charging for the corresponding cycle in mAh. Curve **2305** corresponds to Example 3, curve **2307** corresponds to Comparative Example GG, and curve **2309** corresponds to Comparative Example HH. As shown, Example 3 (curve **1705**) does not exhibit any irregularities and had a final actual capacity (after 60 cycles) with substantially the same capacity after 60 cycles as the nominal areal capacity. This indicates that Example can maintain 80% or more, 85% or more, 90% or more, 95% or more, and/or 98% or more of the initial capacity after 60 cycles or more under these testing conditions. In contrast, Comparative Example FF (curve **2307**) exhibited significant irregularities starting around cycle 7 and eventually failing around cycle 15. Comparative Example GG (curve **2309**) exhibited significant irregularities starting around cycle 8 and eventually failing by cycle 20. Example 3 and Comparative Example GG have the same surface roughness Ra of the first major surface, and Example 3 and Comparative Example HH have the same surface roughness Ra of the second major surface. Consequently, the results in **FIG. 23** and Table 3 demonstrate that the cycling stability and/or capacity retention in unexpectedly increased by the combination of a low surface roughness Ra (e.g., about 0.6 μm or less) of the first major surface and a high surface roughness Ra (e.g., about 1 μm or more) of the second major surface.

[0142] Table 4 presents the properties of Example 4 and Comparative Examples II-KK. Example 4 and Comparative Examples II-KK are the same as Example 2 and Comparative Examples EE-GG except that the anode is lithium metal instead of the lithium alloy. The lithium metal anode was heated at the temperature shown in Table 4 for 5 minutes. Visual inspection of Comparative Examples JJ-KK indicated that the lithium metal at 300°C did not wet the first major surface of the solid-state electrolyte as completely as the metal alloy at 300°C (e.g., Comparative Examples FF-GG). However, visual inspection of Example 4 and Comparative Example II indicated that the lithium metal at 330°C wetted the first major surface of the solid-state electrolyte more completely than the lithium metal at 300°C in Comparative Examples JJ-KK.

Table 4: Properties of Example 4 and Comparative Examples II-KK with lithium metal anode

Example	Anode-side roughness (1 st Major Surface)	Cathode-side roughness (2 nd Major Surface)	Temperature (°C)	Maximum charging current density (mA/cm ²)
4	SiC: 0.4 μm	SiC: 1.2 μm	330°C	1.6*
CE II	SiC: 0.4 μm	SiC: 0.4 μm	330°C	1.0
CE JJ	SiC: 0.4 μm	SiC: 1.2 μm	300°C	0.8
CE KK	SiC: 0.4 μm	SiC: 0.4 μm	300°C	1.0

* = example withstood all charging current densities tested

[0143] **FIGS. 24-27** show capacity-voltage (CV) curves for Example 4 and Comparative Examples II-KK, respectively. For **FIGS. 24-27**, the batteries were tested at a nominal areal capacity of 1 mAh/cm² with a discharging rate of 0.5C at 25°C for all cycles whereas the charging current density (or charging rate) varied. Like Example 2 and Comparative Examples DD-FF, for Example 4 and Comparative Examples II-KK, the charging current density was initially 0.4 mA/cm² (0.4C) and increased by 0.2 mA/cm² (0.2 C) every 10 cycles with the last cycle at a given charging current density (until failure) shown in **FIGS. 24-27** for simplicity, but the maximum charging rate was 1.6C. In **FIGS. 24-27**, the horizontal axis **2401** corresponds to the instantaneous capacity in mAh/cm², and the vertical axis **2403** corresponds to voltage in volts (V). In **FIG. 24**, curves **2405, 2407, 2409, 2411, 2413, 2415, and 2417** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C, 0.6C, 0.8C, 1C, 1.2C, 1.4C, and 1.6C, respectively. Curves **2423** correspond to the charging curves up to 1.6C, which superimpose on one another. All of the curves in **FIG. 24** (including 1.6C) appear normal. In **FIG. 25**, curves **2505, 2507, 2509, and 2511** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C, 0.6C, 0.8C, and 1C, respectively. Curves **2523** correspond to the charging curves at 0.4C, 0.6C, and 0.8C that superimposed on one another, and curve **2525** corresponds to the charging curve at 1C. Curve **2511** exhibited irregularities, and curve **2525** indicates that a short circuit occurred. Comparing **FIGS. 24-25**, batteries with the lithium metal anode heated at 330°C exhibits the same relationship between surface roughness Ra of the second major surface as the batteries with the lithium alloy anode (i.e., the higher roughness – 1 μm or more – second major surface outperforms the lower roughness – 0.6 μm or less – second major surface).

[0144] **FIGS. 26-27** show capacity-voltage (CV) curves for Comparative Examples JJ-KK, respectively. In **FIG. 26**, curves **2605, 2607, and 2609** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C, 0.6C, and 0.8C, respectively. Curves **2623, 2625, and 2627** correspond to the charging curves at 0.4C, 0.6C, and 0.8C, respectively. Curve **2609** exhibits irregularities, and curve **2627** indicates that there was a short circuit at 0.8C. In **FIG. 27**, curves **2705, 2707, 2709, and 2711** correspond to discharging curves at 0.5C as part of the cycles with charging at 0.4C, 0.6C, 0.8C, and 1C, respectively. Curves **2723** correspond to the charging curves 0.4C, 0.6C, and 0.8C that superimpose on one another, and curve **2725** corresponds to the charging curve at 1C. Curve **2711** exhibits irregularities, and curve **2725** indicates reduced charging capacity at 1C. Comparing Example 4 and Comparative Example II with Comparative

Examples JJ-KK, heating the lithium metal at 330°C enabled the batteries to withstand greater charging rates than batteries where the lithium metal was heated at 300°C, which can be attributed to the reduced wettability of the lithium metal on the solid-state electrolyte at 300°C. Consequently, heating a lithium metal anode at greater than 300°C (e.g., 330°C or more) is critical to achieving the improved performance of batteries in accordance with the present disclosure (while this is not the case for lithium alloy anodes).

[0145] The above observations can be combined to provide solid-state electrolytes, batteries, and methods of making the same comprising a surface(s) of the solid-state electrolyte with a predetermined surface roughness Ra. The surface roughness Ra of the first major surface (e.g., facing the anode) of the solid-state electrolyte can be about 0.6 μm or less (e.g., from about 0.1 μm to about 0.5 μm), which can increase a charging rate that the battery can withstand. The surface roughness of the second major surface (e.g., facing the cathode) of the solid-state electrolyte can be about 1 μm or more (e.g., from about 1.2 μm to about 3 μm), which can decrease an interfacial resistance of the battery. Further combining a low surface roughness Ra of the first major surface (e.g., about 0.6 μm or less or from about 0.1 μm to about 0.5 μm) with a high surface roughness Ra of the second major surface (e.g., about 1 μm or more or from about 1.2 μm to about 3 μm) can unexpectedly increase the longevity of the battery and/or the capacity retention of the battery and as demonstrated in the Examples herein. Without wishing to be bound by theory, it is believed that the low roughness (e.g., about 0.6 μm or less or from about 0.1 μm to about 0.5 μm) of the first major surface enables increased charging rates by providing a substantially uniform surface for the anode, which enables uniform contact with the anode, reduces current concentration across the surface, and/or decreases the formation of dendrites. Without wishing to be bound by theory, it is believed that high roughness (e.g., about 1 μm or more or from about 1.2 μm to about 3 μm) of the second major surface decreases interfacial resistance by increasing a surface area of the interface between the solid-state electrolyte and the liquid electrolyte.

[0146] Methods of the present disclosure include polishing the first major surface and/or the second major surface to achieve a predetermined surface roughness Ra. The polishing can comprise etching, mechanical polishing, or a combination thereof. Without wishing to be bound by theory, etching for a short period of time (e.g., about 4 minutes or less) can reduce surface irregularities without increasing a surface roughness of the first major surface (e.g., by etching grain boundaries of the solid-state electrolytes). Without wishing to be bound by theory, etching for a short period of time (e.g., about 4 minutes or less) can reduce surface irregularities without increasing a surface roughness of the first major surface (e.g., by etching grain boundaries of the

solid-state electrolytes). Without wishing to be bound by theory, etching for a longer period of time (e.g., about 7 minutes or more) can increase a surface roughness of the second major surface, for example by etching grain boundaries of the solid-state electrolytes and/or leaching portions of the solid-state electrolyte. Providing a high grit (or low median particle size) abrasive for mechanically polishing the first major surface can produce a low surface roughness of the first major surface.

[0147] Methods and batteries can comprise a lithium-containing anode. In aspects, the lithium-containing anode can be a lithium alloy, which can increase a wettability of the lithium-containing material on the first major surface of the solid-state electrolyte, which enables the battery to withstand high charging rates even when the lithium alloy is heated at 300°C as well as at greater temperatures. In aspects, the lithium-containing anode can consist essentially of lithium metal. Methods of the present disclosure comprise heating the lithium metal at about 330°C or more can enable the lithium metal to wet or otherwise conform to the first major surface, which unexpectedly improves the charging rate that the battery can withstand, as demonstrated by the Examples herein, for example, by providing intimate and/or uniform contact between the lithium metal anode and the first major surface of the solid-state electrolyte.

[0148] Providing a solid-state electrolyte (e.g., in a solid-state battery) can address common safety concerns, for example, leakage, poor chemical stability, and flammability often seen in batteries employing liquid electrolytes. Moreover, providing a solid-state electrolyte can also suppress polysulfide shuttling from the cathode to the anode, thereby leading to improved electrode (e.g., anode, cathode) utilization and a high discharge capacity and energy density. Providing a solid-state electrolyte can reduce a formation of dendrites (e.g., lithium dendrites) that can otherwise result in failure of the battery. Providing an interlayer comprising a liquid electrolyte can wet the interface between the cathode and the solid-state electrolyte to reduce interfacial resistance therebetween while minimizing a total amount of liquid electrolyte in the solid-state battery.

[0149] Directional terms as used herein—for example, up, down, right, left, front, back, top, bottom—are made only with reference to the figures as drawn and are not intended to imply absolute orientation.

[0150] It will be appreciated that the various disclosed aspects may involve features, elements, or steps that are described in connection with that aspect. It will also be appreciated that a feature, element, or step, although described in relation to one aspect, may be interchanged or combined with alternate aspects in various non-illustrated combinations or permutations.

[0151] It is also to be understood that, as used herein the terms “the,” “a,” or “an,” mean “at least one,” and should not be limited to “only one” unless explicitly indicated to the contrary. For example, reference to “a component” comprises aspects having two or more such components unless the context clearly indicates otherwise. Likewise, a “plurality” is intended to denote “more than one.”

[0152] As used herein, the term “about” means that amounts, sizes, formulations, parameters, and other quantities and characteristics are not and need not be exact, but may be approximate and/or larger or smaller, as desired, reflecting tolerances, conversion factors, rounding off, measurement error and the like, and other factors known to those of skill in the art. Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, aspects include from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. Whether or not a numerical value or endpoint of a range in the specification recites “about,” the numerical value or endpoint of a range is intended to include two aspects: one modified by “about,” and one not modified by “about.” It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint and independently of the other endpoint.

[0153] The terms “substantial,” “substantially,” and variations thereof as used herein are intended to note that a described feature is equal or approximately equal to a value or description. For example, a “substantially planar” surface is intended to denote a surface that is planar or approximately planar. Moreover, as defined above, “substantially similar” is intended to denote that two values are equal or approximately equal. In aspects, “substantially similar” may denote values within about 10% of each other, for example, within about 5% of each other, or within about 2% of each other.

[0154] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is in no way intended that any particular order be inferred.

[0155] While various features, elements, or steps of particular aspects may be disclosed using the transitional phrase “comprising,” it is to be understood that alternative aspects, including those that may be described using the transitional phrases “consisting of” or “consisting essentially of,” are implied. Thus, for example, implied alternative aspects to an apparatus that comprises

A+B+C include aspects where an apparatus consists of A+B+C and aspects where an apparatus consists essentially of A+B+C. As used herein, the terms “comprising” and “including”, and variations thereof shall be construed as synonymous and open-ended unless otherwise indicated.

[0156] The above aspects, and the features of those aspects, are exemplary and can be provided alone or in any combination with any one or more features of other aspects provided herein without departing from the scope of the disclosure.

[0157] It will be apparent to those skilled in the art that various modifications and variations can be made to the present disclosure without departing from the spirit and scope of the disclosure. Thus, it is intended that the present disclosure cover the modifications and variations of the aspects herein provided they come within the scope of the appended claims and their equivalents.

What is claimed is:

1. A battery, comprising:
 - a lithium-containing anode;
 - a solid-state electrolyte comprising a first major surface facing the lithium-containing anode and a second major surface opposite the first major surface, the first major surface comprising a surface roughness R_a of 0.6 micrometers or less, and the second major surface comprising a surface roughness of 1 micrometer or more;
 - a liquid electrolyte disposed on the second major surface of the solid-state electrolyte; and
 - a cathode disposed over the second major surface of the solid-state electrolyte, the liquid electrolyte positioned between the second major surface and cathode.
2. The battery of claim 1, wherein the surface roughness R_a of the first major surface ranges from 0.1 micrometers to 0.5 micrometers.
3. The battery of claim 1, wherein the surface roughness R_a of the second major surface ranges from 1.2 micrometers to 3 micrometers.
4. The battery of claim 1, wherein an interfacial resistance between the cathode and the lithium-containing anode is $60 \Omega \text{ cm}^2$ or less at 25°C .
5. The battery of claim 1, wherein an interfacial resistance of the battery is 50% or less than an interfacial resistance of another battery identical to the battery but with the first major surface and the second major surface switched.
6. The battery of any one of claims 1-5, wherein the battery can withstand at least 10 cycles at a charging current density of 1.6 mA/cm^2 or more to a capacity of 1 mAh/cm^2 with a discharge rate of 0.5 mA/cm^2 at 25°C , where the area is based on a surface area of the lithium-containing anode.
7. The battery of claim 6, wherein another battery identical to the battery but with the first major surface and the second major surface switched cannot withstand 10 cycles at a charging

current density of 1.25 mA/cm² to the capacity of 1 mAh/cm² with the discharge rate of 0.5 mA/cm² at 25°C.

8. The battery of any one of claims 1-5, wherein the battery comprises a capacity retention of 90% or more after 60 cycles at a charging rate of 0.5C and a discharging rate of 0.17 C to a maximum capacity of 3 mAh/cm² with a cutoff voltage of 4.5V and at 60°C, and the area is based on a surface area of the lithium-containing anode.

9. The battery of any one of claims 1-5, wherein the cathode comprises at least one of lithium cobaltite (LCO), lithium manganite spinel (LMO), lithium nickel cobalt aluminate (NCA), lithium nickel manganese cobalt oxide (NCM) (LiNi_dCo_eMn_{1-d-e}O₂, where 0 < d < 1, 0 < e < 1), lithium iron phosphate (LiFePO₄) (LFP), lithium cobalt phosphate (LCP), lithium titanate, lithium niobium tungstate, lithium nickel manganate, and lithium titanium sulfide (LiTiS₂), or combinations thereof.

10. The battery of any one of claims 1-5, wherein the solid-state electrolyte comprises at least one of:

- (i) Li_{7-3a}La₃Zr₂LaO₁₂, with L = Al, Ga, or Fe and 0 < a < 0.33;
- (ii) Li₇La_{3-b}Zr₂M_bO₁₂, with M = Bi or Y and 0 < b < 1;
- (iii) Li_{7-c}La₃(Zr_{2-c}N_c)O₁₂, with N = In, Si, Ge, Sn, V, W, Te, Nb, or Ta and 0 < c < 1;
- (iv) protonated LLZO (e.g., H_xLi_{6.5-x}La₃Zr_{1.5}Al_{0.5}O₁₂, with I = In, Si, Ge, Sn, V, W, Te, Nb, or Ta and 0 < x < 4 or H_xLi_{6.25-x}E_{0.25}La₃Zr₂O₁₂, with E = Al, Ga, or Fe and 0 < x < 4); or a combination thereof.

11. A method of forming a battery comprising:

polishing a first major surface of a solid-state electrolyte to form a surface roughness Ra of 0.6 micrometers or less;

polishing a second major surface of the solid-state electrolyte to form a surface roughness Ra of 1 micrometer or more, the second major surface opposite the first major surface;

heating a lithium-containing precursor to a temperature of 300°C or more to form a lithium-containing anode disposed on the first major surface; and

disposing the solid-state electrolyte over a cathode, the second major surface of the solid-state electrolyte facing the cathode.

12. The method of claim 11, wherein the heating the lithium-containing precursor comprises heating to a temperature from 330°C to 400°C for from 5 minutes to 10 minutes, and the lithium-containing anode consists essentially of lithium metal.
13. The method of claim 11, wherein the polishing the first major surface comprises mechanical polishing with a grit size of 1000 or more.
14. The method of any one of claims 11-13, wherein polishing the second major surface comprises mechanical polishing with a grit size of 600 or less.
15. The method of any one of claims 11-13, wherein the polishing the first major surface comprises etching in an acidic solution comprising a concentration from 0.1 molar to 3 molar for 4 minutes or less.
16. The method of any one of claims 11-13, wherein the polishing the second major surface comprising etching in an acidic solution comprising a concentration from 0.1 molar to 3 molar for from 7 minutes to 30 minutes.
17. The method of any one of claims 11-13, further comprising disposing a liquid electrolyte on the cathode such that the liquid electrolyte is positioned between the cathode and the second major surface, the liquid electrolyte comprising a lithium-containing salt.
18. The method of any one of claims 11-13, wherein the surface roughness Ra of the first major surface ranges from 0.1 micrometers to 0.5 micrometers.
19. The method of any one of claims 11-13, wherein the surface roughness Ra of the second major surface range from 1.2 micrometers to 3 micrometers.
20. The method of any one of claims 11-13, wherein an interfacial resistance of the battery is 50% or less than an interfacial resistance of another battery identical to the battery but with the first major surface and the second major surface switched.

1/13

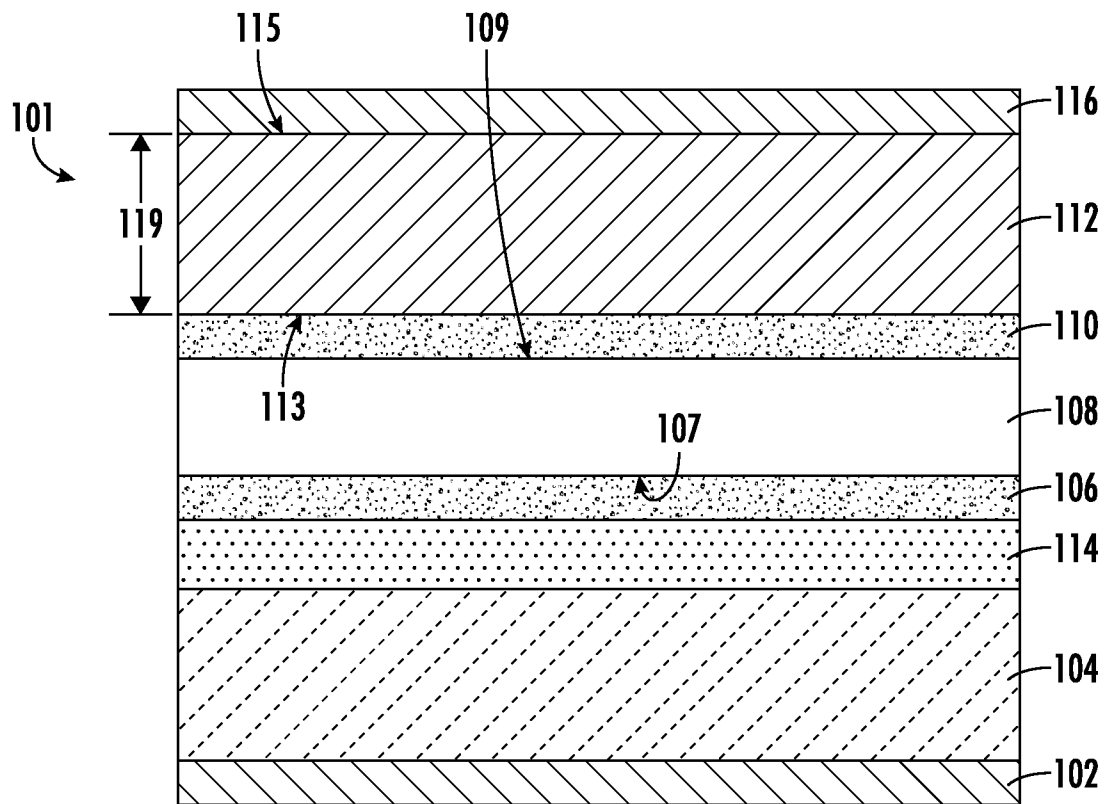


FIG. 1

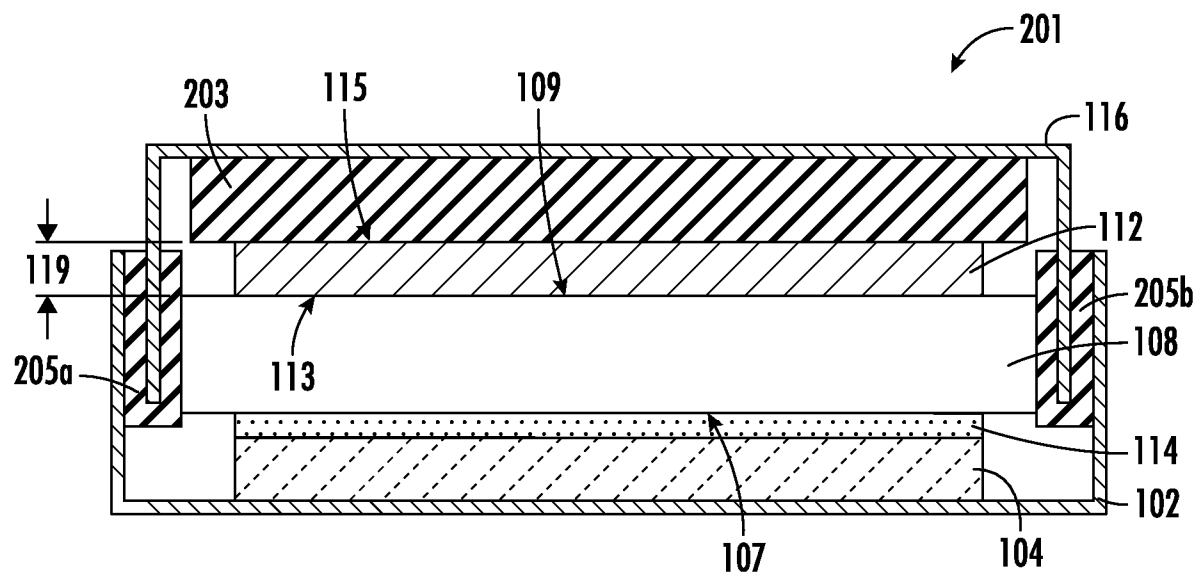


FIG. 2

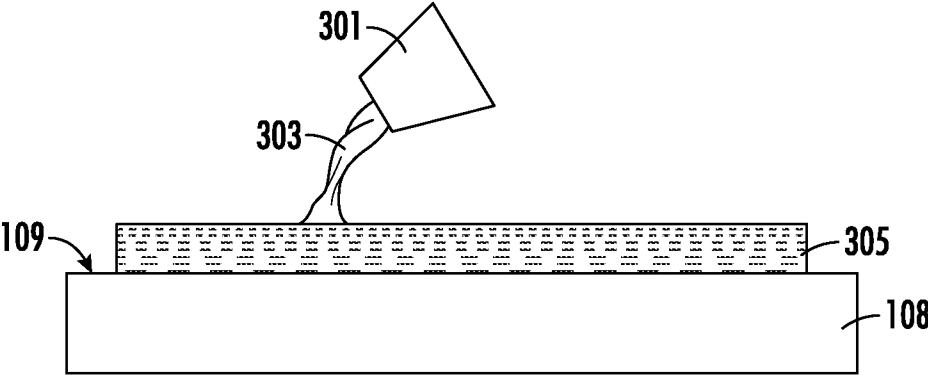


FIG. 3

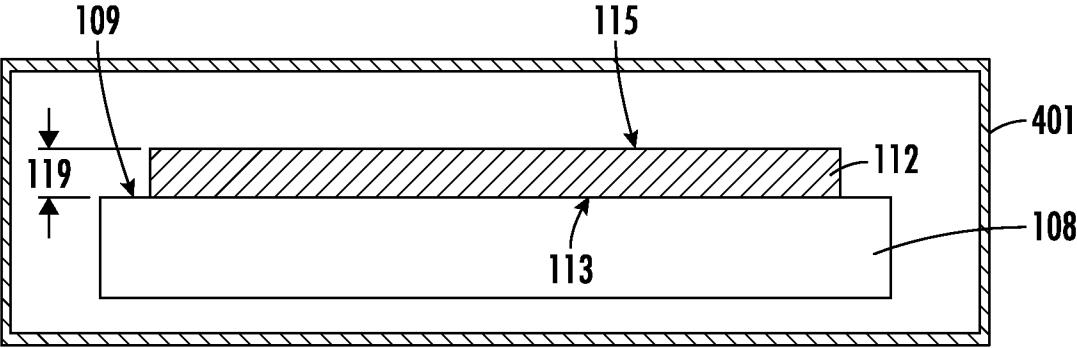


FIG. 4

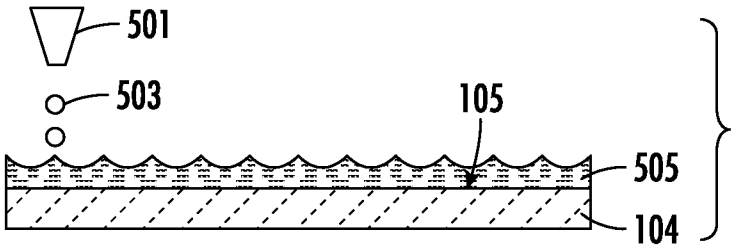


FIG. 5

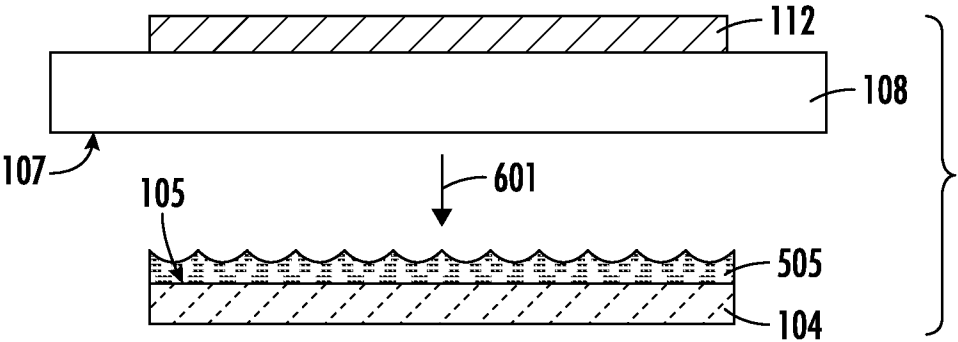


FIG. 6

4/13

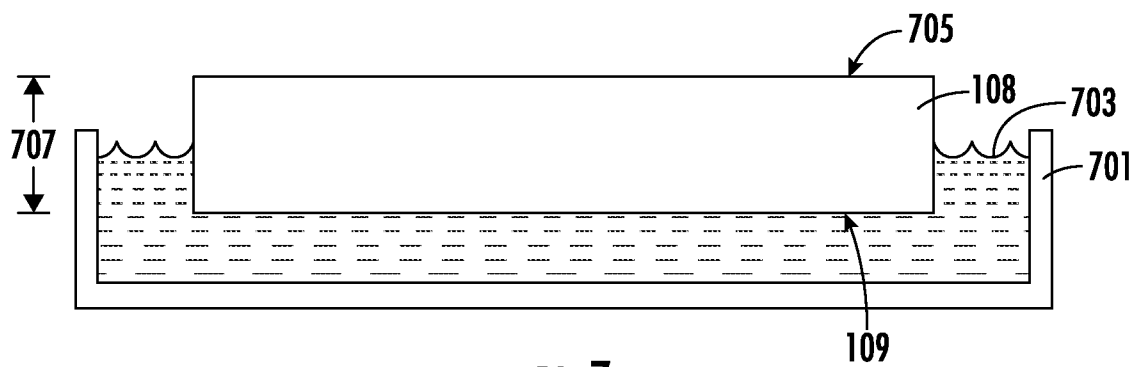


FIG. 7

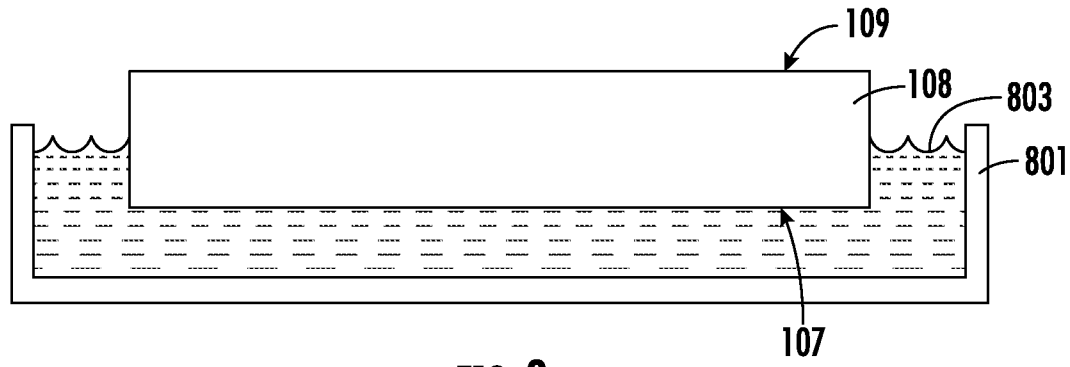


FIG. 8

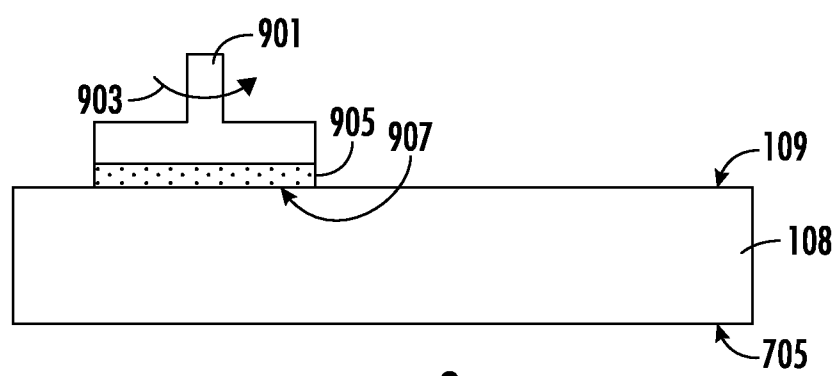


FIG. 9

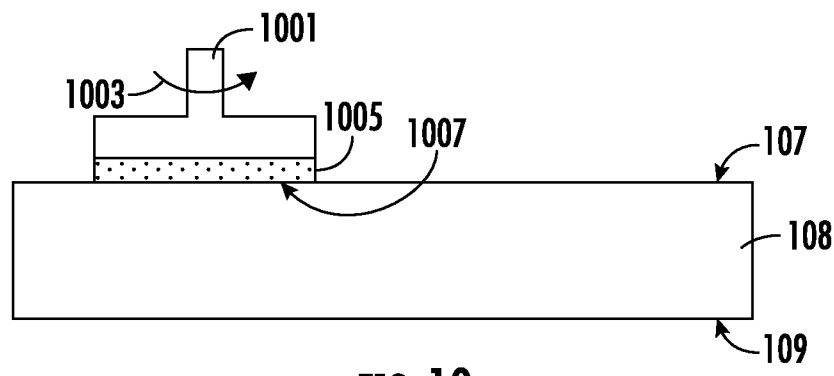
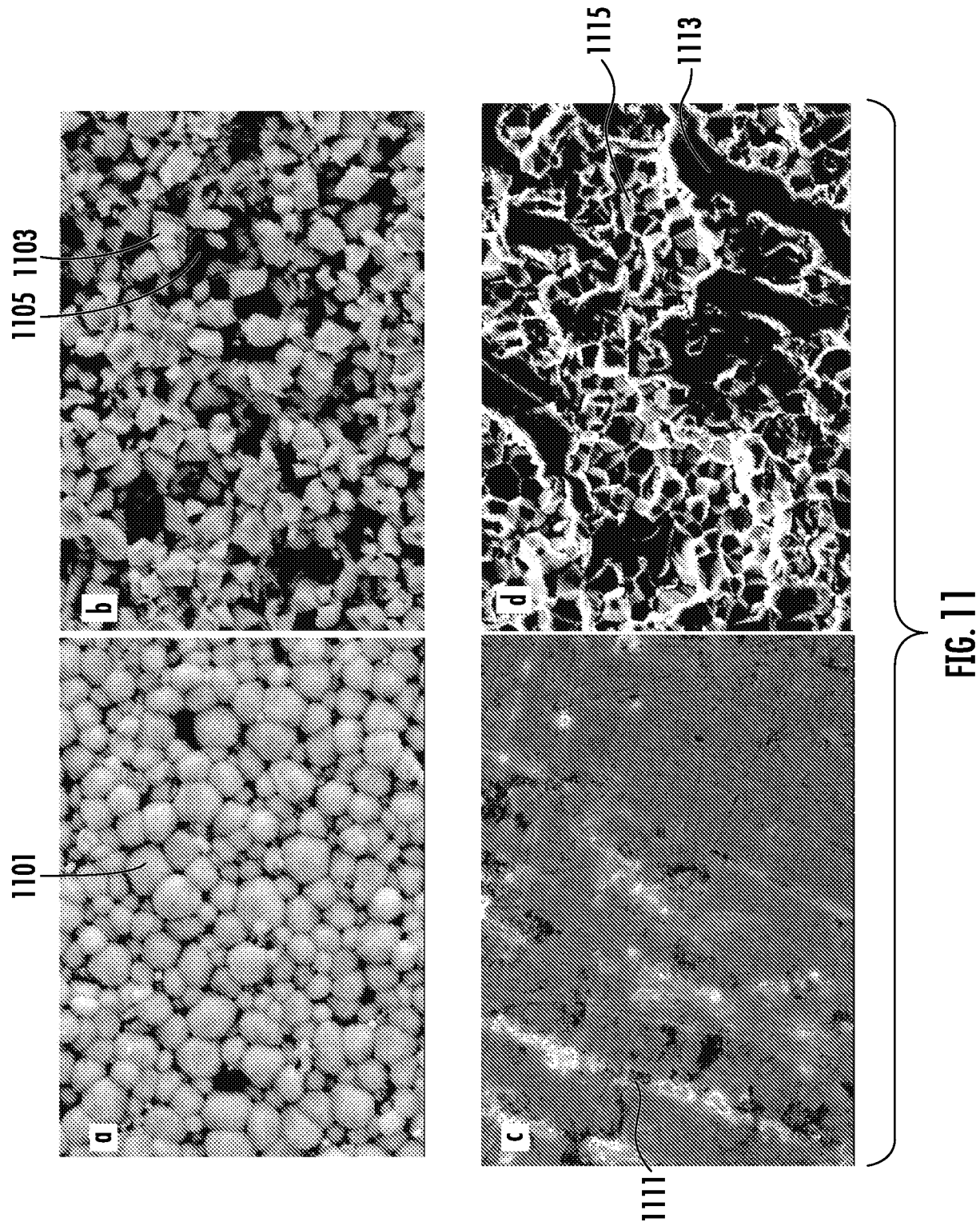
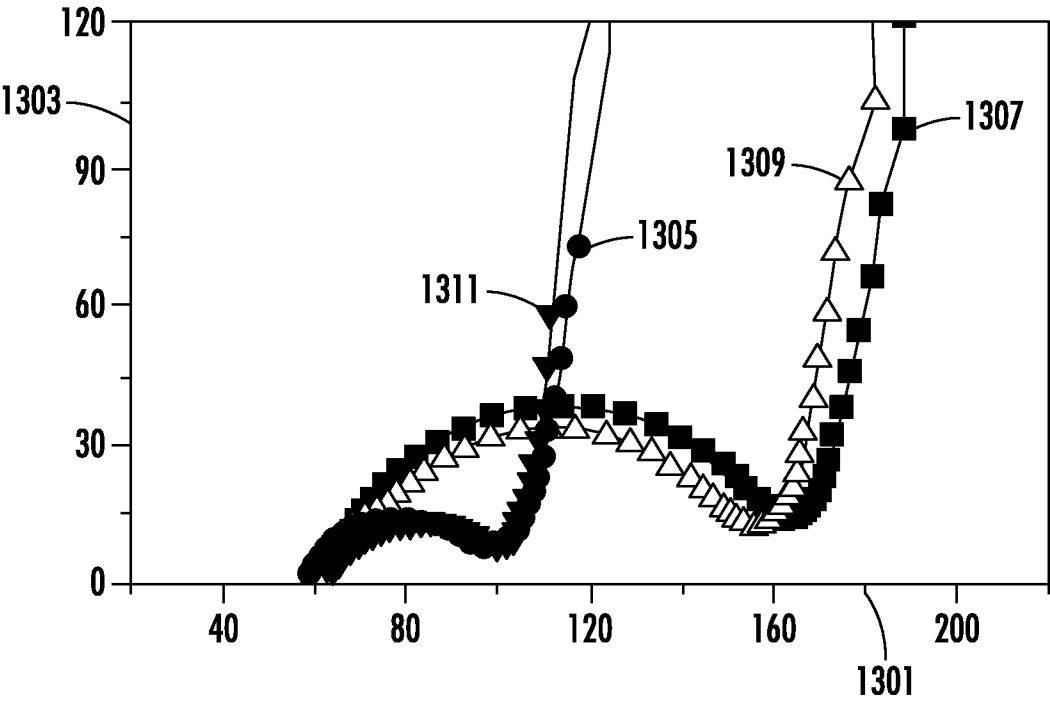
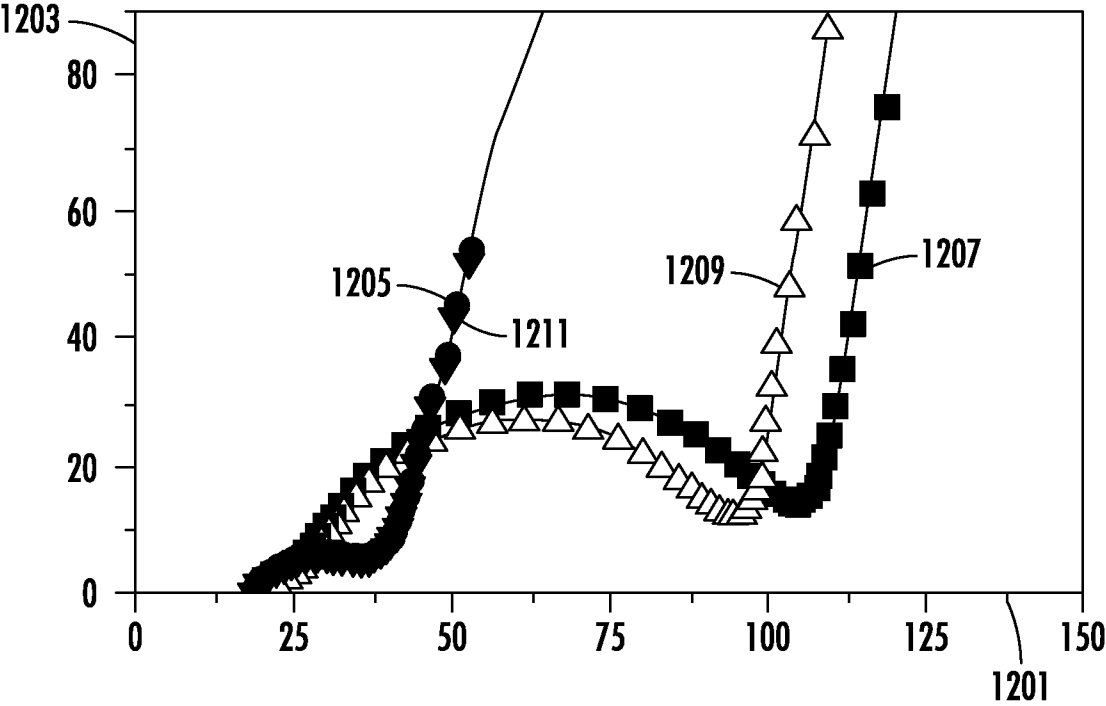


FIG. 10



6/13



7/13

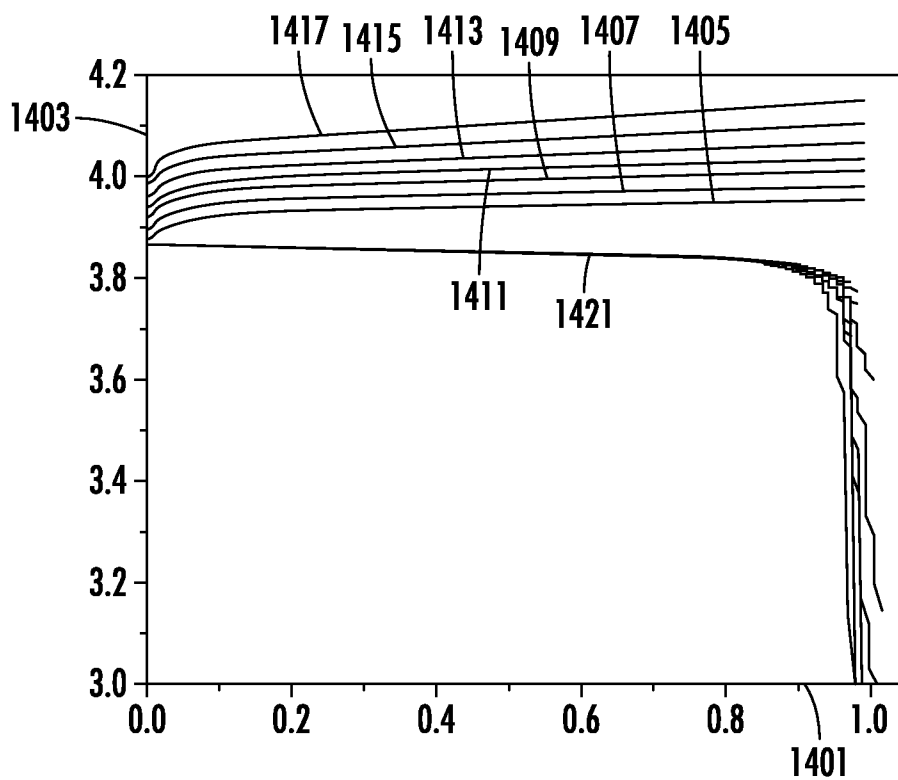


FIG. 14

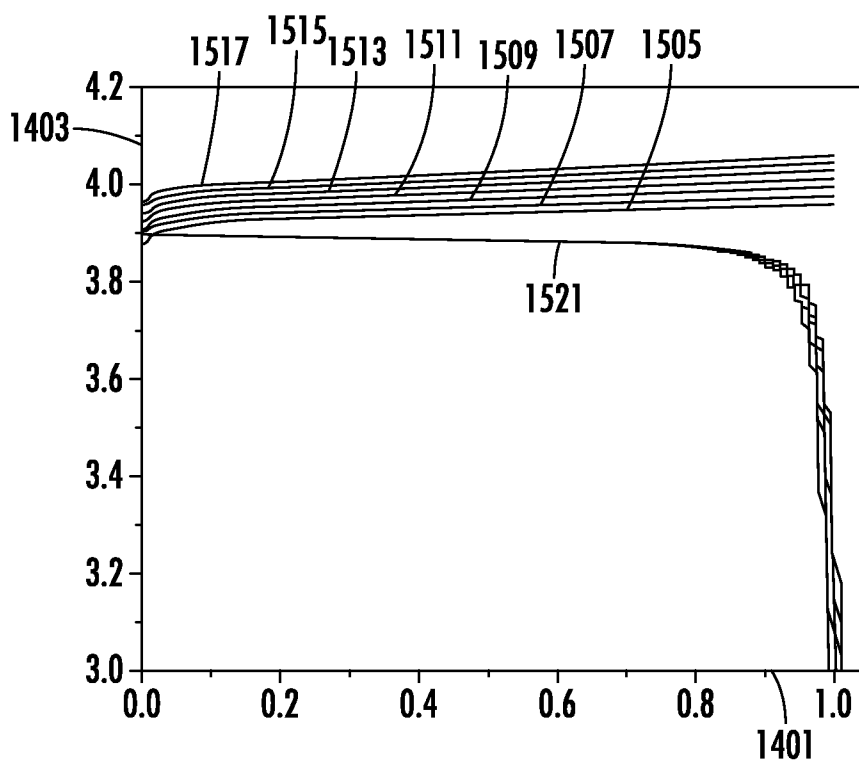


FIG. 15

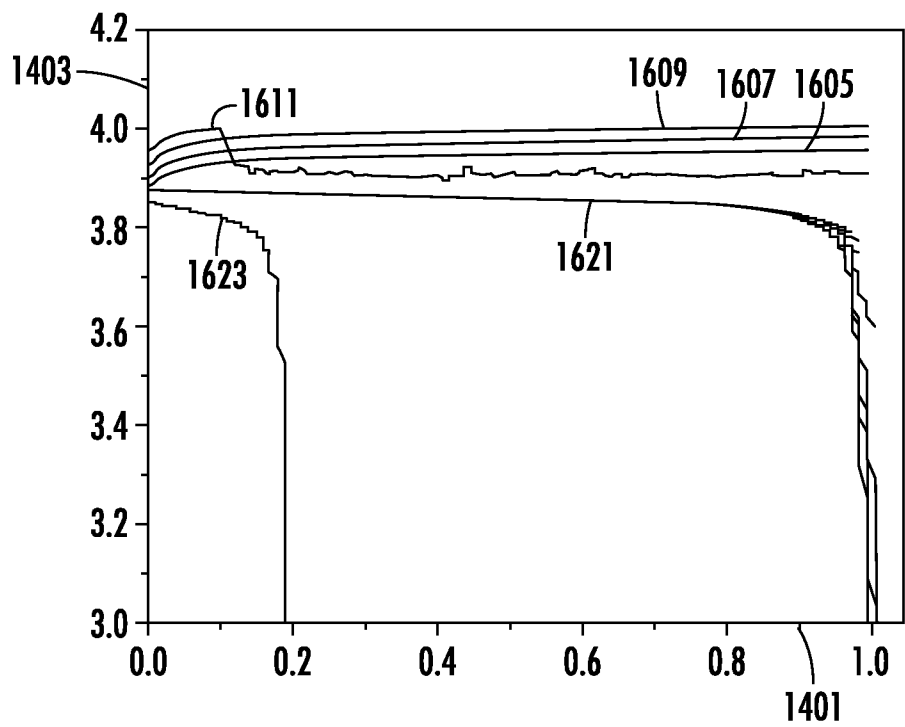


FIG. 16

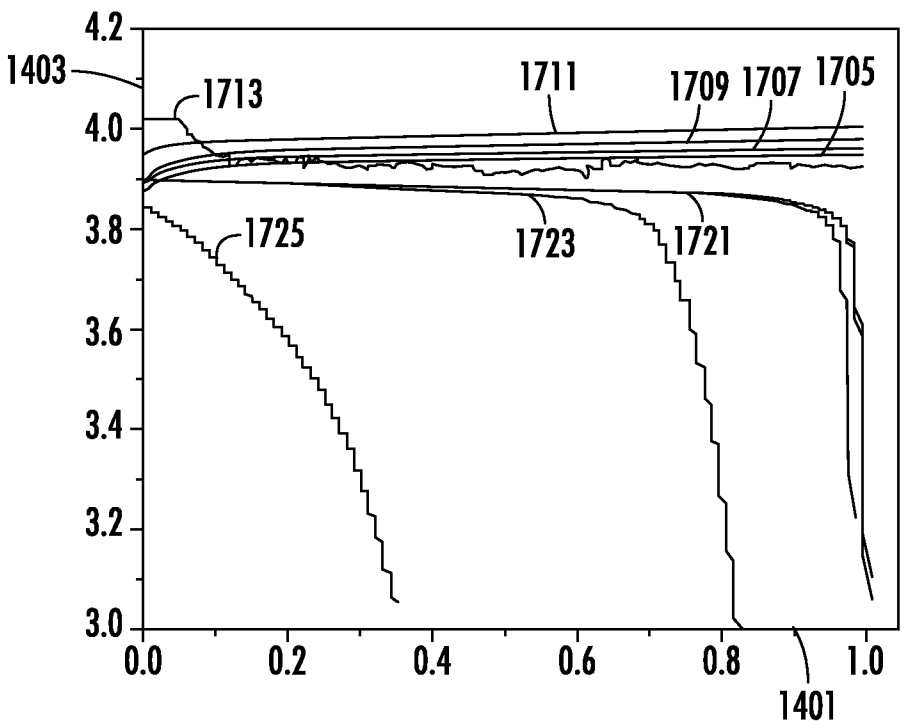


FIG. 17

9/13

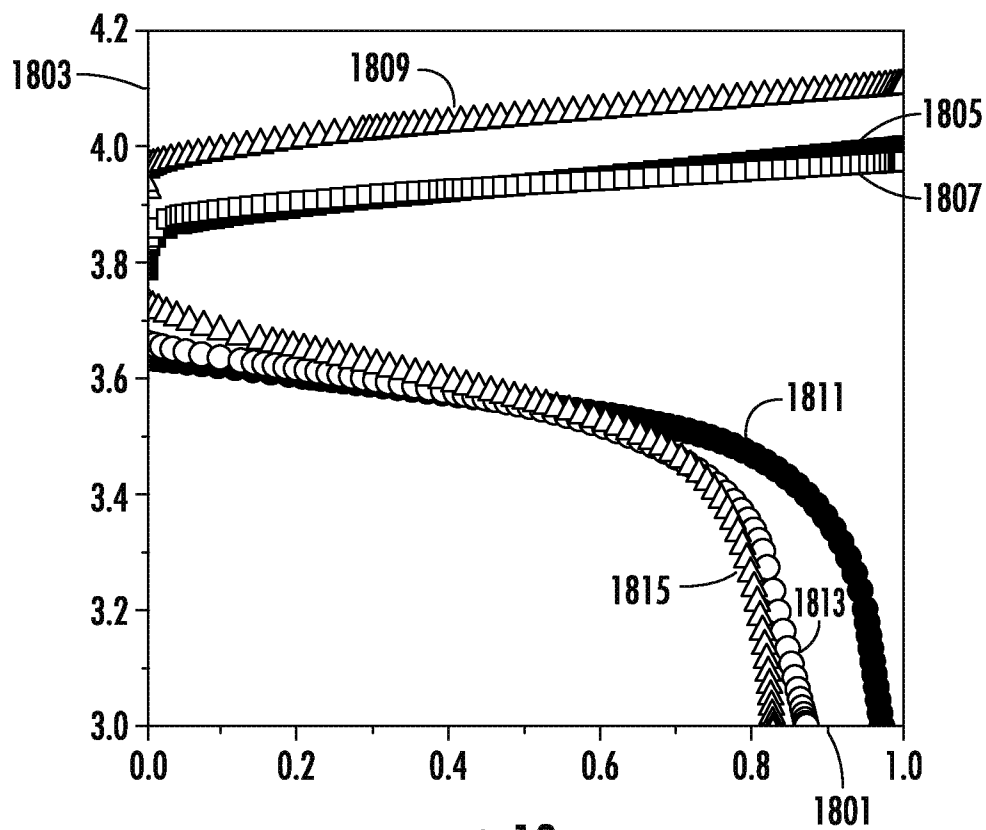


FIG. 18

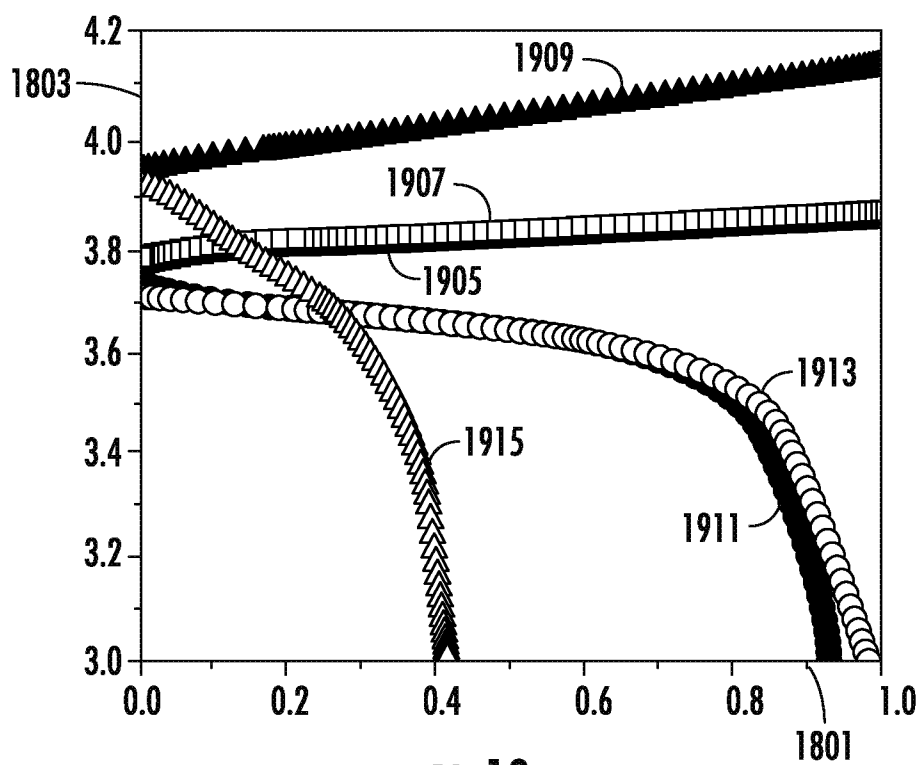


FIG. 19

10/13

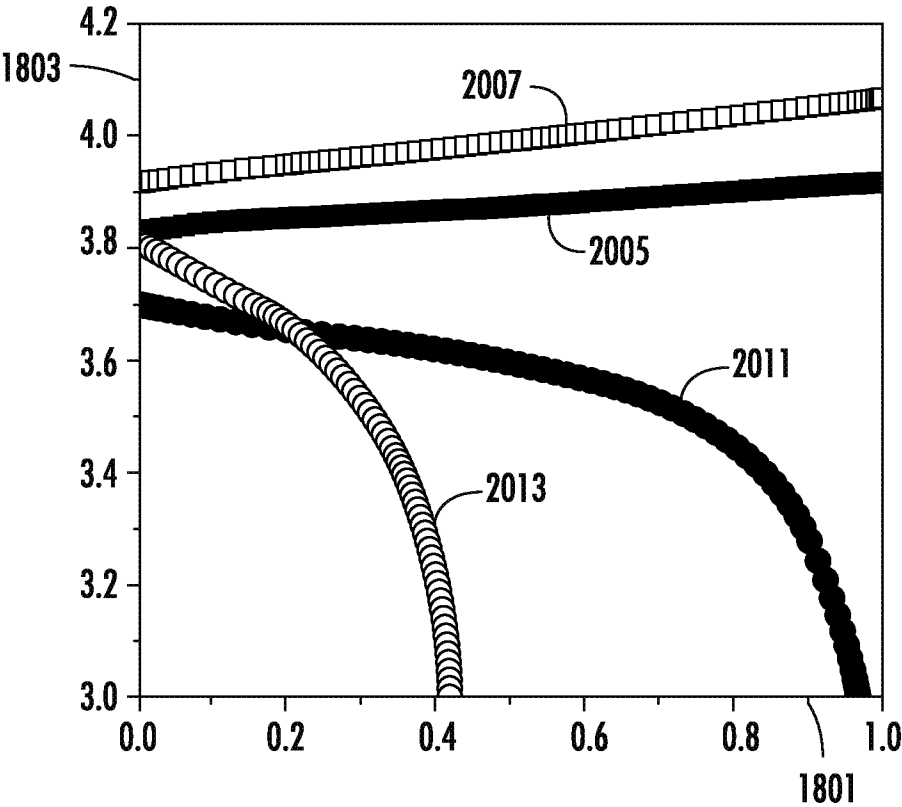


FIG. 20

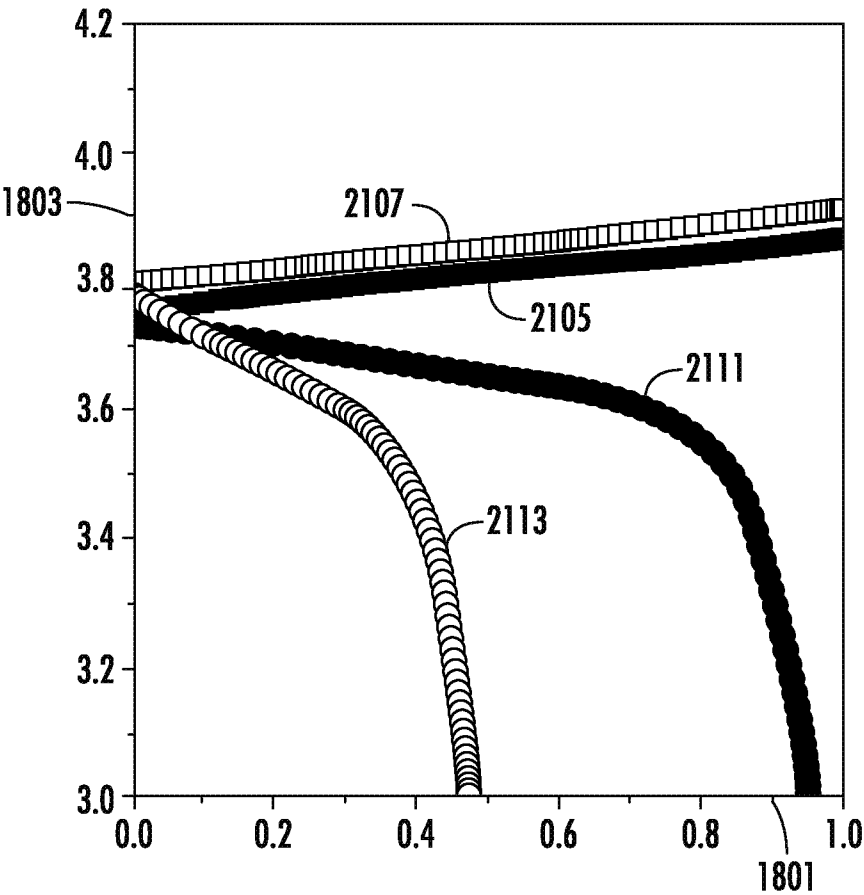
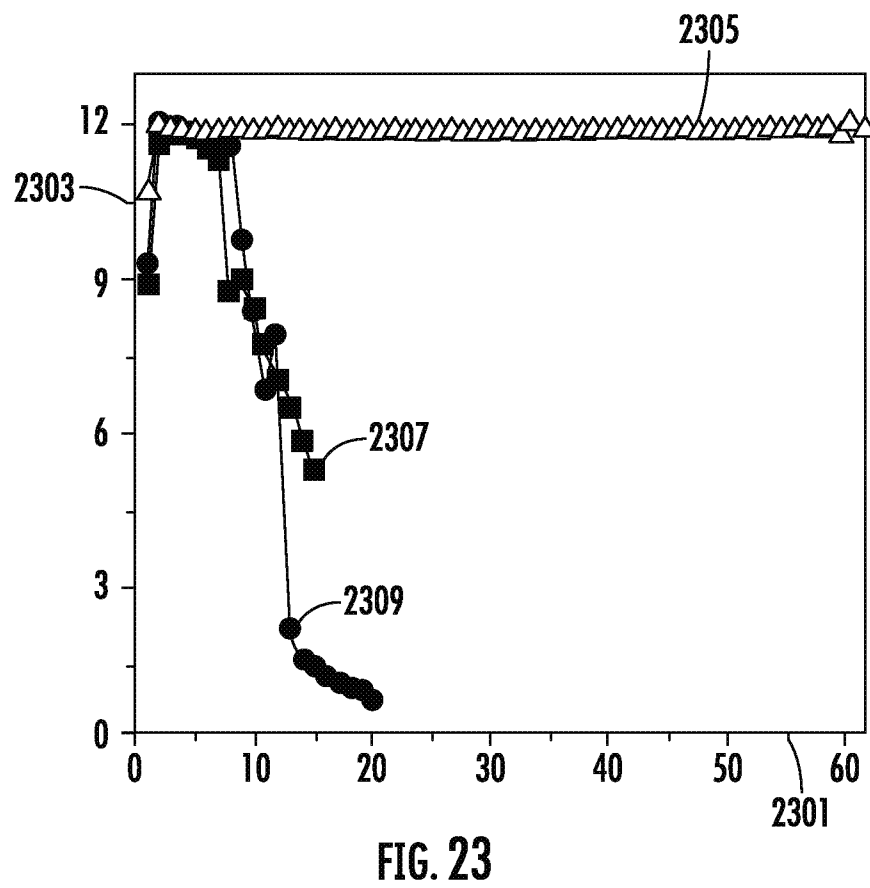
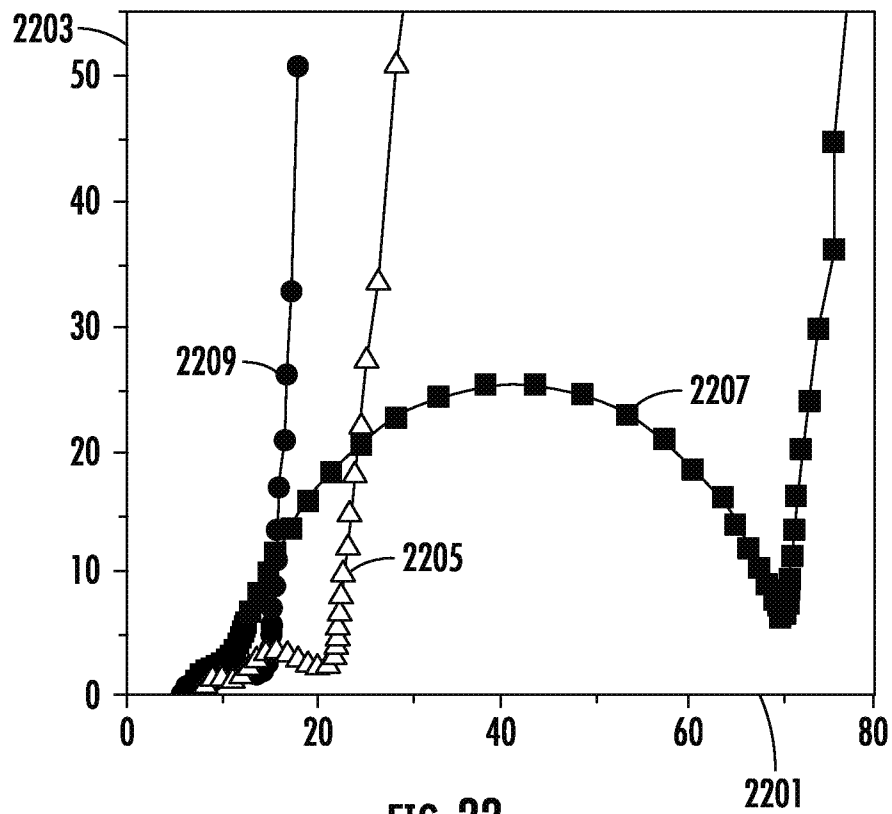


FIG. 21

11/13



12/13

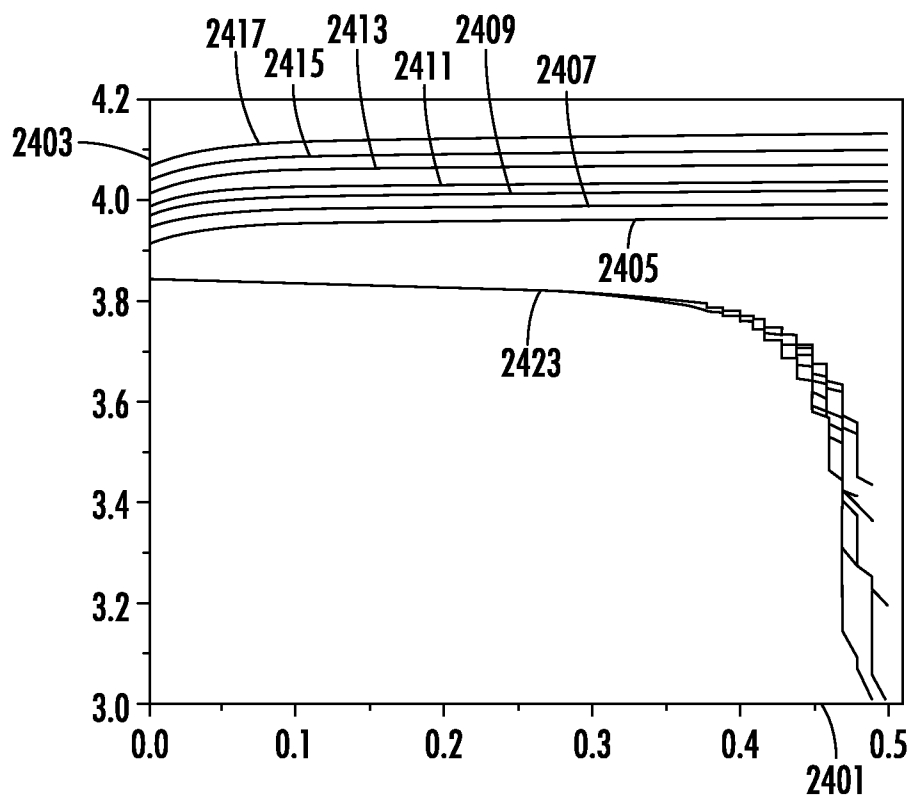


FIG. 24

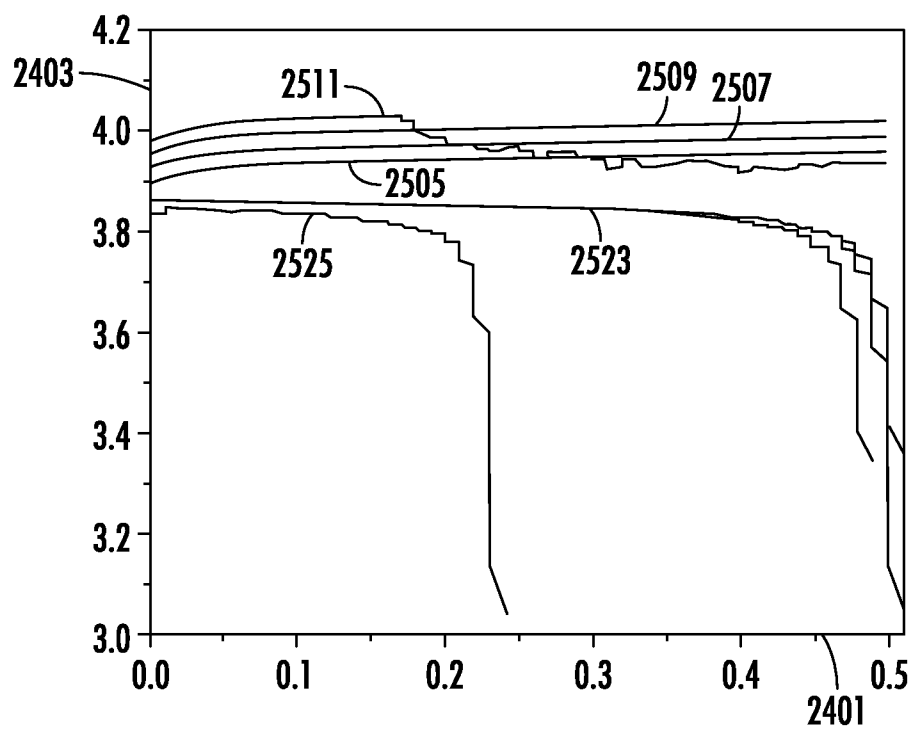


FIG. 25

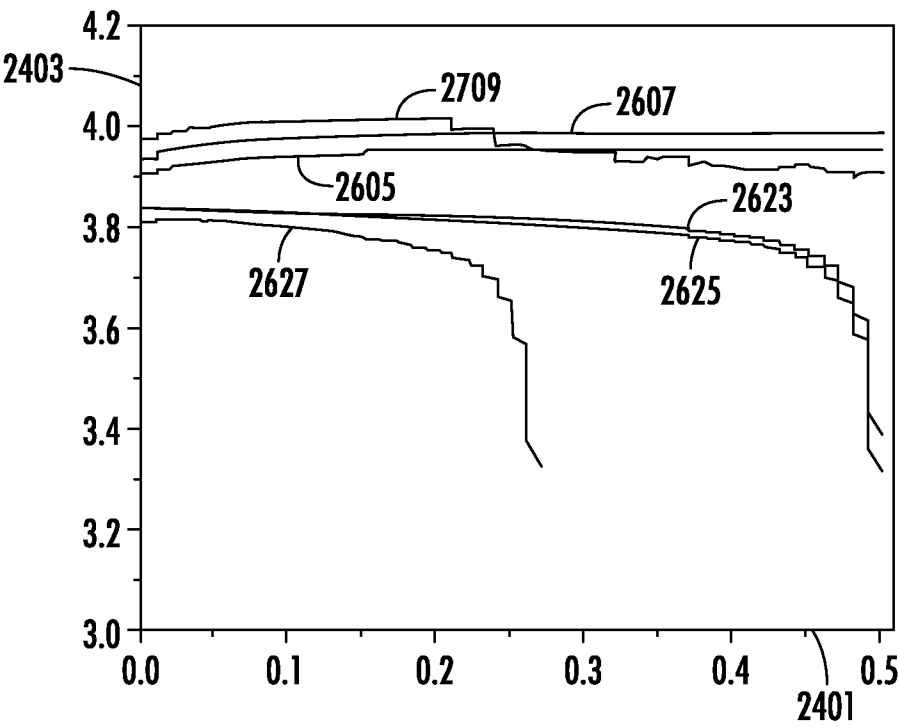


FIG. 26

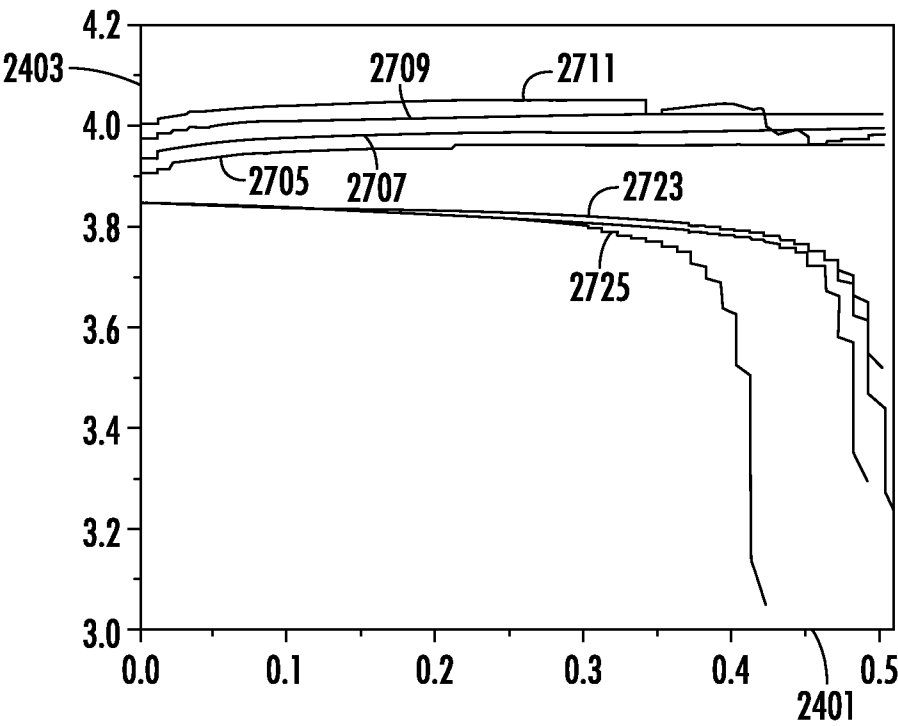


FIG. 27

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/21834

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

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

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

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

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

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

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

Group I: Claims 1-10 are directed to a battery.

Group II: Claims 11-20 are directed to a method of forming a battery.

---see extra sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-10

Remark on Protest

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/21834

A. CLASSIFICATION OF SUBJECT MATTER

IPC - INV. H01M 10/0525, H01M 10/0562, H01M 10/0566 (2024.01)
 ADD. H01M 4/04 (2024.01)

CPC - INV. H01M 10/0525, H01M 10/0562, H01M 10/0566

ADD. H01M 4/04, H01M 2300/0065, H01M 2300/0094, Y02E 60/10

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

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

See Search History document

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

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2022/0399532 A1 (QINGTAO (KUNSHAN) ENERGY DEVELOPMENT CO., LTD.) 15 December 2022 (15.12.2022) entire document; especially Fig. 1; para [0028], para [0052]-[0055], para [0095]	1-10
Y	US 2021/0399331 A1 (THE REGENTS OF THE UNIVERSITY OF MICHIGAN) 23 December 2021 (23.12.2021) entire document; especially para [0018]-[0019], para [0030]	1-10
A	US 2020/0395584 A1 (QUANTUMSCAPE CORPORATION) 17 December 2020 (17.12.2020) entire document	1-10

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

11 July 2024

Date of mailing of the international search report

JUL 30 2024

Name and mailing address of the ISA/US

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

Facsimile No. 571-273-8300

Authorized officer

Kari Rodriguez

Telephone No. PCT Helpdesk: 571-272-4300

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 24/21834

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

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

Special Technical Features:

Group I includes the special technical feature of a liquid electrolyte disposed on the second major surface of the solid-state electrolyte, not included in the other group.

Group II includes the special technical feature of polishing and heating, not included in the other group.

Common Technical Features:

The only technical feature shared by Groups I-II that would otherwise unify the groups is a battery comprising: a solid-state electrolyte comprising a first major surface facing the lithium-containing anode and a second major surface opposite the first major surface, the first major surface comprising a surface roughness Ra of 0.6 micrometers or less, and the second major surface comprising a surface roughness of 1 micrometer or more, a cathode disposed over the second major surface of the solid-state electrolyte. However, this shared technical feature does not represent a contribution over the prior art, because the shared technical feature is disclosed by US 2022/0399532 A1 to QingTao (KunShan) Energy Development Co., Ltd. (hereinafter "QingTao").

Qingtao discloses a battery comprising: a solid-state electrolyte (3) comprising a first major surface facing the lithium-containing anode (1b) and a second major surface opposite the first major surface, the first major surface comprising a surface roughness Ra of 0.6 micrometers or less, and the second major surface comprising a surface roughness of 1 micrometer or more, a cathode (2) disposed over the second major surface of the solid-state electrolyte (3) (Fig. 1; para [0028]- the numerical range of the surface roughness of the first solid-state electrolyte is 0.1 μm to 30 μm ; para [0052]-[0055]- the negative electrode active material includes any one or a combination of at least two of a metallic active material, a carbon active material or an oxide active material...the oxide active material includes $\text{Li}_4\text{Ti}_5\text{O}_{12}$; para [0095]- an all-solid-state battery...The first solid-state electrolyte 3 is located between the positive electrode 2 and the first negative electrode 1 b).

Accordingly, the inventions listed as Groups above lack unity of invention under PCT Rule 13 because they do not share a same or corresponding special technical feature providing contribution over prior art.