$Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$, pristine/doped $Li_7La_3Zr_2O_{12}$ (LLZO), and $LiCoO_2$, exhibited an improved performance, but they were still limited by the Li ion diffusion bottleneck introduced by the solid electrolyte pellet/layer utilized.

Reengineering Li-S hybrid quasi-solid system by controlling the solid component microstructure could help to overcome its current limitations. A study has shown that porous $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ can achieve remarkably good Li-S hybrid battery performance. However, the porous solid electrolyte used in this study was fabricated using typical solid-state synthesis, which is energy-demanding, requiring 2 calcination steps at 900 °C and 1200 °C, labor-intensive, involving ball milling, calcination, mixing, pressing, and sintering, and time-consuming, requiring about 3 days. In addition, ceramic electrolyte pellets are known to be brittle and susceptible to cracking during processing, especially when they are porous.

There is therefore a need to provide a material that overcomes or at least ameliorates, one or more of the disadvantages described above.

Summary

In an aspect, there is provided a material comprising a garnet-type oxide in the form of a powder comprising a plurality of sheet structures, wherein the material comprises a solid mixture of at least lithium and oxygen.

In an ~~aspect~~example, there is provided a material comprising a garnet-type oxide in the form of a powder comprising a plurality of sheet structures.

Advantageously, the garnet-type oxide may be $Li_7La_3Zr_2O_{12}$ (LLZO).

In another aspect there is provided a method for forming the material as defined above, the method comprising the steps of mixing a plurality of precursors of a garnet-type oxide comprising at least lithium and oxygen in an aqueous solvent in the presence of a sugar to form a sol, and heating the sol

In another ~~aspect~~example, there is provided a method for forming the material as defined above, the method comprising the steps of: mixing a plurality of precursors for a garnet-type oxide in an aqueous solvent in the presence of a sugar to form a sol; and heating the sol.

Advantageously, a novel sol-gel methodology was developed for the synthesis of garnet-type oxide sheets, such as LLZO sheets, which were used as building blocks for the construction of a 3D garnet-type oxide or LLZO framework that was imbibed with liquid electrolyte, forming a high-performance HQSE. The garnet-type oxide or LLZO sheets were synthesized via a “cupcake” method, which is a novel one-step sol-gel process utilizing sucrose as a complexing and structure-directing agent to derive the garnet-type oxide or LLZO precursor with sheet-like morphology. The disclosed method has the following advantages:

- Cost effectiveness: Unlike typical energy/time-consuming solid-state reaction methods that are used for garnet-type oxide or LLZO synthesis, the disclosed method may be facile, short and

achieve the desired crystal structure and morphology at a relatively low temperature, making it cost effective. The reason why less energy and time may be expended using the disclosed method is because of its sol-gel nature, where the precursors are mixed at the molecular level, making it easier for the reactants to form the desired phase. This is unlike conventional solid-state reactions, where the reactions are started using solid precursors that require significantly longer time, greater labour and higher energy to achieve a reaction and the right crystal structure. In addition, the raw materials for garnet-type oxide or LLZO are not expensive. For example, a

rough estimation for the raw materials for the synthesis of 100 g of LLZO sheets is approximately 376 SGD based on lab-scale non-bulk prices (for example from Sigma-Aldrich) and this could be much lower if bulk orders are used.

- Scalability: The disclosed method may be scalable, where the precursors and structure directing agent are simply mixed together by dissolving them in deionized water. This is followed by a two-step reaction that takes place using a single program in a furnace. Around 0.5 g may be synthesized per batch, and there is no limitation to scaling the method up to produce larger batches.

- Versatility of binders: The role of the binder is to bind the garnet-type oxide or LLZO sheets together forming the 3D HQSE solid framework. In addition to polytetrafluoro-ethylene (PTFE), other polymeric binders may be used, such as polyvinylidene fluoride, polyethylene oxide, sodium alginate, sodium carboxymethyl cellulose, polyacrylic acid, LA-132 (a copolymer comprising acrylamide, lithium carboxylate acrylonitrile), poly(acrylonitrile-methyl methacrylate) and styrene butadiene rubber/carboxy methyl cellulose.

In another aspect, there is provided a hybrid quasi-solid electrolyte framework comprising the material as defined above and a polymer.

In another aspect, there is provided a method for forming the hybrid quasi-solid electrolyte framework as defined above, the method comprising the step of mixing a material as defined above with a polymer to form a framework mixture.

In an ~~aspect~~example, there is provided a hybrid quasi-solid electrolyte comprising the hybrid quasi-solid electrolyte framework as defined above and an electrolyte.

In an aspect, there is provided a hybrid quasi-solid electrolyte comprising the hybrid quasi-solid electrolyte framework as defined above and an electrolyte dissolved in an electrolyte solvent.

Advantageously, the hybrid quasi-solid electrolyte may have a controlled microstructure and be used in Li hybrid quasi-solid batteries. The hybrid quasi-solid electrolyte may comprise a 3D garnet-type oxide such as a $Li_7La_3Zr_2O_{12}$ (LLZO) sheet-based solid framework imbibed with liquid electrolyte. Advantageously, $Li_7La_3Zr_2O_{12}$ (LLZO) may be chosen as the garnet-type oxide due to its high ionic conductivity (cubic phase), and good chemical and electrochemical stability.

Advantageously, the hybrid quasi-solid electrolyte may have high Li ion conductivity, excellent compatibility with a Li metal anode, impressive thermal stability, enhanced anodic stability, and excellent battery performance. A remarkable Li-S battery rate capability (about 515 and about 340 mAh/g at 1C and 2C, respectively) was achieved at a loading density of 1.5 mg cm^{-2}, which is among the best achieved by Li-S hybrid quasi-solid batteries. The 3D sheet-based framework was found to be critical for optimal battery performance. Moreover, the Li-S hybrid quasi-solid system showed an outstanding stability against extreme temperature conditions.

Advantageously, the hybrid quasi-solid garnet-type oxide or LLZO hybrid quasi-solid electrolyte circumvented the conventional electrolyte leakage problem, ensured adequate contact with electrodes, and enhanced stability against the Li metal anode. In addition, it

Claims

1. A material comprising a garnet-type oxide in the form of a powder comprising a plurality of sheet structures, wherein the material comprises a solid mixture of at least lithium and oxygen.

2. The material according to claim 1, wherein the sheet structures are interconnected with each other.

3. The material according to claim 1 or 2, wherein the material further comprises ~~a solid mixture of at least lithium and oxygen and optionally~~ an element selected from the group consisting of magnesium, aluminium, silicon, calcium, scandium, vanadium, manganese, iron, nickel, gallium, germanium, strontium, yttrium, zirconium, niobium, barium, tantalum, lanthanum, cerium, neodymium, samarium, europium, gadolinium, terbium and any mixture thereof.

4. The material according to claim 3, wherein the material is further doped with one or more elements selected from the group consisting of hydrogen, beryllium, boron, carbon, sodium, phosphorous, sulfur, chlorine, potassium, titanium, chromium, cobalt, copper, zinc, arsenic, selenium, bromine, rubidium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, iodine, cesium, hafnium, tungsten, iridium, platinum, gold, mercury, thallium, lead, bismuth, and any mixture thereof.

5. The material according to any one of the preceding claims, wherein the material comprises a solid mixture of lithium, lanthanum, zirconium and oxygen, preferably having a lithium:lanthanum:zirconium:oxygen ratio of 7:3:2:12.

6. The material according to any one of the preceding claims, wherein the sheet structures have a lateral dimension of greater than 1 µm and a thickness in the range of ~~about~~ 100 nm to ~~about~~ 250 nm.

7. The material according to any one of the preceding claims, wherein the sheet structures are crystalline.

8. A method for forming the material according to any one of claims 1 to 7, the method comprising the steps of:

   mixing a plurality of precursors of a garnet-type oxide comprising at least lithium and oxygen in an aqueous solvent in the presence of a sugar to form a sol, and heating the sol.

9. The method according to claim 8, wherein the method is a sol-gel method.

10. The method according to claim 8 or 9, wherein the precursors are selected from at least a lithium salt and oxygen or a compound comprising oxygen and optionally a compound comprising an element selected from the group consisting of magnesium, aluminium, silicon,

calcium, scandium, vanadium, manganese, iron, nickel, gallium, germanium, strontium, yttrium, zirconium, niobium, barium, tantalum, lanthanum, cerium, neodymium, samarium, europium, gadolinium, terbium and any mixture thereof, wherein the compound is preferably a salt of the element as valency allows.

11. The method according to claim 10, further comprising the step of incorporating a dopant into the material, the dopant being one or more elements selected from the group consisting of hydrogen, beryllium, boron, carbon, sodium, phosphorous, sulfur, chlorine, potassium, titanium, chromium, cobalt, copper, zinc, arsenic, selenium, bromine, rubidium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, iodine, cesium, hafnium, tungsten, iridium, platinum, gold, mercury, thallium, lead, bismuth, and any mixture thereof.

12. The method according to claim 10 or 11, wherein the mixing step comprises mixing a lithium salt, a lanthanum salt, and a zirconium salt with the sugar, wherein the salt is nitrate, preferably wherein the lanthanum salt is $La(NO_3)_3.6H_2O$, and the zirconium salt is $ZrO(NO_3)_2.xH_2O$, wherein x is 0 or an integer in the range of 1 to 10.

13. The method according to any one of claims 8 to 12, wherein the aqueous solvent is deionized water.

14. The method according to any one of claims 8 to 13, wherein the sugar is a monosaccharide, a disaccharide, an oligosaccharide or any mixture thereof, preferably selected from the group consisting of glucose, fructose, galactose, sucrose, lactose, maltose, glycans, carbohydrates, starch and cellulose.

15. The method according to any one of claims 9 to 14, wherein the sol gel has a pH in the range of ~~about~~ 1 to ~~about~~ 2.

16. The method according to any one of claims 8 to 15, wherein the heating step comprises a first heating step and a second heating step, wherein the first heating step is performed at a temperature in the range of ~~about~~ 150 °C to ~~about~~ 500 °C, and a duration in the range of 0.5 hours to 5 hours, or more than 5 hours, and the second heating step is performed at a temperature in the range of ~~about~~ 600 °C to ~~about~~ 1500 °C, and a duration in the range of ~~about~~ 30 minutes to ~~about~~ 10 hours, or more than 10 hours, to decompose the sugar.

17. The method according to any one of claims 8 to 16, comprising the step of breaking up the heated sol to obtain a powder.

18. A hybrid quasi-solid electrolyte framework comprising the material according to any one of claims 3 to 7 and a polymer.

19. The hybrid quasi-solid electrolyte framework of claim 18, wherein the polymer is selected from the group consisting of polytetrafluoroethylene (PTFE), polyvinylidene fluoride, polyethylene oxide, sodium alginate, sodium carboxymethyl cellulose, polyacrylic acid, poly(acrylonitrile-methyl methacrylate), styrene butadiene rubber/carboxy methyl cellulose

(SBR/CMC), a copolymer comprising acrylamide, lithium carboxylate and acrylonitrile and any mixture thereof.

20. The hybrid quasi-solid electrolyte framework of claim 18 or 19, wherein the ratio between the hybrid quasi-solid electrolyte framework:polymer is in the range of ~~about~~ 20:1 to ~~about~~ 2:1 by weight.

21. The hybrid quasi-solid electrolyte framework of any one of claims 18 to 20, wherein the framework is in the form of a disc having a diameter in the range of ~~about~~ 10 mm to ~~about~~ 20 mm or more than 20 mm and the thickness of the disc is in the range of ~~about~~ 50 µm to ~~about~~ 500 µm or more than 500 µm.

22. The hybrid quasi-solid electrolyte framework according to any one of claims 18 to 21, wherein the framework is porous.

23. A method for forming the hybrid quasi-solid electrolyte framework according to any one of claims 18 to 22, the method comprising the step of mixing a material of any one of claims 3 to 7 with a polymer to form a framework mixture.

24. The method according to claim 23, comprising the step of rolling the framework mixture into a membrane having a thickness in the range of ~~about~~ 50 µm to ~~about~~ 500 µm or more than 500 µm and the step of cutting the membrane into a disc having a diameter in the range of 10 mm to 20 mm or more than 20 mm.

25. The method according to claim 23 or 24, comprising the step of drying the framework mixture at a temperature in the range of ~~about~~ 50 °C to ~~about~~ 100 °C.

26. A hybrid quasi-solid electrolyte comprising the hybrid quasi-solid electrolyte framework of any one of claims 18 to 22 and an electrolyte dissolved in an electrolyte solvent.

27. The hybrid quasi-solid electrolyte according to claim 26, wherein the electrolyte is present in the electrolyte solvent at a concentration in the range of ~~about~~ 0.25 M to ~~about~~ 10 M.

28. The hybrid quasi-solid electrolyte according to claim 26 or 27, wherein the electrolyte comprises a lithium compound, preferably selected from the group consisting of $LiPF_6$, $LiClO_4$, $LiAsF_6$, $LiBF_4$, lithium trifluoromethanesulfonate and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI).

29. The hybrid quasi-solid electrolyte according to any one of claims 26 to 28, wherein the electrolyte solvent is selected from the group consisting of ether, carbonate and any mixture thereof, preferably selected from the group consisting of dimethoxyethane (DME), 1,3-dioxolane (DOL), propylene carbonate, ethylene carbonate , dimethyl carbonate and diethyl carbonate, preferably a mixture of DME and DOL, or a mixture of ethylene carbonate and diethylcarbonate.

30. The hybrid quasi-solid electrolyte according to claim 29, wherein the ratio of DME to DOL,

or the ratio of ethylene carbonate and diethylcarbonate is in the range of ~~about~~ 0.25:1 to ~~about~~ 1:0.25 by volume.

31. The hybrid quasi-solid electrolyte according to any one of claims 26 to 30, wherein the electrolyte further comprises an electrolyte additive, preferably $LiNO_3$, and the additive is present at a concentration in the range of ~~about~~ 1 wt% to ~~about~~ 3 wt%.

32. A method for preparing the hybrid quasi-solid electrolyte according to any one of claims 26 to 31, the method comprising the step of contacting the hybrid quasi-solid electrolyte framework of any one of claims 18 to 22 with an electrolyte.

33. An electrochemical cell comprising the hybrid quasi-solid electrolyte of any one of claims 26 to 31, a cathode and an anode.

34. The electrochemical cell according to claim 33, wherein the cathode is selected from the group consisting of a sulfur cathode, sulfur carbon/ceramic cathode and metal cathode.

35. The electrochemical cell according to claim 33 or 34, wherein the cathode is selected from a graphene/sulfur cathode or a $LiCoO_2$ cathode.

36. The electrochemical cell according to claim 35, wherein the cathode is a graphene/sulfur cathode and the hybrid quasi-solid electrolyte comprises 1 M LiTFSI in DME:DOL (1:1 by volume) and 2 wt% $LiNO_3$, at 5 µL/mg to 50 µL/mg sulfur, or the cathode is a $LiCoO_2$ cathode and the hybrid quasi-solid electrolyte comprises 1 M $LiPF_6$ in ethylene carbonate:diethylcarbonate (1:1 by volume) at 5 µL/mg to 50 µL/mg $LiCoO_2$.

37. The electrochemical cell according to any one of claims 33 to 35, wherein the anode comprises a material selected from the group consisting of lithium metal, graphite, hard carbon, silicon, tin, silicon/C composite, tin/C composite and any mixture thereof.

38. A method of manufacturing an electrochemical cell according to any one of claims 33 to 37, the method comprising the step of contacting the hybrid quasi-solid electrolyte of any one of claims 26 to 31 with a cathode and an anode.

39. Use of the hybrid quasi-solid electrolyte framework according to any one of claims 18 to 22 as a separator in an electrochemical cell.