

A solid-state electrolyte

Technical Field

The present invention relates to an improved solid-state electrolyte.

5 Background

All-solid-state batteries have been identified as being capable of the next generation of energy storage in view of their inherent safety features while in use. In that respect, lithium-ion conducting oxides have been shown to be good solid electrolytes. However, there remains the problem of compatibility of the solid electrolytes with the cathode and
10 the anode in battery construction.

There is therefore a need for an improved solid-state electrolyte.

Summary of the invention

The present invention seeks to address these problems, and/or to provide an improved solid-state electrolyte.

15 According to a first aspect, there is provided a solid-state electrolyte comprising a composite of a lithium ion conducting oxide and a polymer matrix, wherein the electrolyte has an ionic conductivity at 25°C of ≥ 1 mS/cm. In particular, the electrolyte has an ionic conductivity at 25°C of ≥ 1.5 mS/cm.

The lithium ion conducting oxide may be any suitable lithium ion conducting oxide.

20 According to a particular aspect, the lithium ion conducting oxide may comprise at least one lithium ion polyanion oxide. In particular, the lithium ion conducting oxide may comprise $\text{Li}_x(\text{MO}_{6/2})_m(\text{TO}_{4/2})_t$ polyanion oxide, wherein:

M represents a cation M^{a+} , M being selected from the group consisting of: Ta, Nb, Ti, Mo, W, V, Zr, Hf, Ge, Bi, Cr, Sb, In, Fe, Ga, and $3 \leq a \leq 6$;

25 T represents a cation T^{b+} , T being selected from the group consisting of: P, Si, Al, Ge, S, B, Pb, Mo, W, As, Se, Te, Mn, Sn, Zn, and $2 \leq b \leq 6$;

$1 \leq m \leq 20$;

$1 \leq t \leq 20$; and

x is $(6 - a) \times m + (4 - b) \times t$. Even more in particular, the lithium ion conducting oxide

30 comprises LiTa_2PO_8 (LTPO).

The polymer matrix comprised in the electrolyte may be any suitable polymer matrix.

The weight ratio of the lithium ion conducting oxide to the polymer matrix comprised in the electrolyte may be any suitable ratio. For example, the electrolyte may comprise 1-50% lithium ion conducting oxide by weight based on the total weight of the electrolyte.

5 The electrolyte may be in any suitable form. According to a particular aspect, the electrolyte may be in the form of a film. The film may have a suitable thickness. For example, the film may have a thickness of $\geq 1 \mu\text{m}$.

According to a second aspect, there is provided a solid-state battery comprising a cathode, an anode, and a solid-state electrolyte according to the first aspect.

The battery may be any suitable battery. For example, the battery may be a Li-S battery.

10 A third aspect provides a method of preparing the solid-state electrolyte according to the first aspect, the method comprising:

- mixing a lithium ion conducting oxide with a polymer matrix to obtain a mixture;
- applying the mixture on a surface of a substrate; and
- curing the mixture coated on a surface of a substrate to form the electrolyte.

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The method may be performed in a suitable environment. According to a particular aspect, the method may be performed in an inert environment.

The mixing may comprise mixing the lithium ion conducting oxide and the polymer matrix in a suitable weight ratio based on the total weight of the mixture. For example, the mixing
20 may comprise mixing the lithium ion conducting oxide in a weight ratio of 1-50 wt % based on the total weight of the mixture.

The applying may comprise applying the mixture by any suitable method.

The curing may comprise curing the mixture under suitable conditions and for a pre-determined period. For example, the curing may be under ultraviolet (UV) light.

25 According to a particular aspect, the pre-determined period may be ≤ 12 hours.

The method may further comprise removing the electrolyte from the surface of the substrate on which the electrolyte is formed. The removing may be by any suitable method.

The method may further comprise: forming the lithium ion conducting oxide prior to the mixing and/or forming the polymer matrix prior to the mixing.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect
5 there shall now be described by way of non-limitative example only exemplary
embodiments, the description being with reference to the accompanying illustrative
drawings. In the drawings:

Figure 1 shows X-ray diffraction pattern for LTPO samples prepared according to one
embodiment of the present invention;

10 Figure 2 shows Nyquist plot of LTPO samples prepared according to one embodiment
of the present invention;

Figure 3 shows DSC curves of electrolyte according to one embodiment of the present
invention;

Figure 4 shows galvanostatic cycling curves of a battery comprising electrolyte according
15 to one embodiment of the present invention;

Figure 5 shows change of resistance of the battery comprising electrolyte according to
one embodiment of the present invention;

Figure 6 shows charge-discharge curves of a battery comprising electrolyte according to
one embodiment of the present invention;

20 Figure 7 shows variation of capacity of a batter comprising electrolyte according to one
embodiment of the present invention with number of cycles;

Figure 8 shows cyclic voltammetry curves of a battery comprising electrolyte according
to one embodiment of the present invention;

Figure 9 shows charge-discharge curves of a battery comprising electrolyte according to
25 one embodiment of the present invention; and

Figure 10 shows capacity of battery comprising electrolyte according to one embodiment
of the present invention.

Detailed Description

As explained above, there is a need for an improved solid electrolyte, particularly for use in an all-solid-state battery.

In general terms, the present invention provides a solid electrolyte composite. As it is a solid electrolyte, it improves the safety of a battery in which it is used. The electrolyte also has high ionic conductivity at room temperature. Further, the method of forming the electrolyte is a low-cost method making it easy to scale up.

According to a first aspect, there is provided a solid-state electrolyte comprising a composite of a lithium ion conducting oxide and a polymer matrix, wherein the electrolyte has an ionic conductivity at 25°C of ≥ 1 mS/cm. In particular, the ionic conductivity may be ≥ 1.5 mS/cm.

The lithium ion conducting oxide may be any suitable lithium ion conducting oxide, particularly a surface-active lithium ion conductive oxide. According to a particular aspect, the lithium ion conducting oxide may comprise at least one lithium ion polyanion oxide. For example, the lithium ion conducting oxide may comprise $\text{Li}_x(\text{MO}_{6/2})_m(\text{TO}_{4/2})_t$ polyanion oxide, wherein:

M represents an octahedrally coordinated network modifier cation such as M^{a+} , M being selected from the group consisting of: Ta, Nb, Ti, Mo, W, V, Zr, Hf, Ge, Bi, Cr, Sb, In, Fe, Ga, and $3 \leq a \leq 6$;

T represents a tetrahedrally coordinated network former cation such as cation T^{b+} , T being selected from the group consisting of: P, Si, Al, Ge, S, B, Pb, Mo, W, As, Se, Te, Mn, Sn, Zn, and $2 \leq b \leq 6$;

$1 \leq m \leq 20$;

$1 \leq t \leq 20$; and

x is $(6 - a) \times m + (4 - b) \times t$. Even more in particular, the lithium ion conducting oxide comprises LiTa_2PO_8 (LTPO).

It is known that LTPO, for example, that total conductivity for LTPO may be up to about 7×10^{-4} S/cm while bulk conductivity for fully dense LTPO may be about 2.8×10^{-3} S/cm. LTPO is also known to be stable over a wide range of temperature, as well as have chemical stability in air, aqueous solution and organic solvents, making it a suitable electrolyte.

The polymer matrix comprised in the electrolyte may be any suitable polymer matrix. For the purposes of the present invention, reference to polymer matrix may refer to a polymer matrix comprising a polymer or a copolymer. According to a particular aspect, the polymer matrix may comprise at least polymers with: non-polar heteroatom groups, such as but not limited to $-O-$; polar groups such as but not limited to $-CF$, $-COOH$, $-C=O$, $-C\equiv N$; charged groups such as but not limited to where Li^+ acts as counter ion; and multi-type of ionic conductive groups, as well as co-polymers and blends of these. For example, the polymer matrix may comprise, but is not limited to: polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), poly(ethyleneoxide) (PEO), poly(formaldehyde) (POM), poly(vinylpyrrolidone) (PVP), poly(ethylenecarbonate) (PEC), polypropylcarbonate (PPC), poly(vinylidene fluoride) (PVDF), co-polymers and blends thereof.

The polymer matrix may comprise a polymer formed from at least one type of monomer. In particular, the at least one type of monomer may be, but not limited to, bisphenol A ethoxylate dimethacrylate (Bis-EMA).

The electrolyte may comprise a suitable amount of the lithium ion conducting oxide and the polymer matrix. For example, the lithium ion conducting oxide comprised in the electrolyte may be 1-50 wt % based on the total weight of the electrolyte. In particular, the electrolyte may comprise 5-45 wt %, 10-40 wt %, 15-35 wt %, 20-30 wt % lithium ion conducting oxide based on the total weight of the electrolyte. According to a particular aspect, the weight ratio of the lithium ion conducting oxide to the polymer matrix comprised in the electrolyte may be 0.3:0.7 based on the total weight of the electrolyte.

The electrolyte comprises a polymer matrix in which the lithium-ions that have been chelated by electron-rich oxygen of the polymer. The lithium ions may be very mobile and may therefore contribute to increasing ionic conductivity of the electrolyte. In particular, in the polymer matrix of the electrolyte, the effect of grain boundary may be removed and total resistance may be observed. The coordinated lithium ions may migrate between or within polymer segments and chains within the matrix as the lithium-oxygen bonds are broken/formed. At the same time, the polymer segments may rearrange and move to transport the lithium ions over longer distances. The increase in the amorphous region in the polymer matrix may increase the movement of the lithium ions in the electrolyte, thereby improving the conductivity of the electrolyte comprising

the polymer matrix in combination with the lithium ions as compared to an electrolyte comprising just the lithium ions without the polymer matrix.

The electrolyte may be in any suitable form. According to a particular aspect, the electrolyte may be in the form of a film. The film may have a suitable thickness. The
5 thickness may be compatible with the thicknesses of separators in conventional Li-based batteries. For example, the film may have a thickness of $\geq 1 \mu\text{m}$, particularly $1\text{-}500 \mu\text{m}$, even more particularly $5\text{-}50 \mu\text{m}$. In particular, the thickness may be $\geq 10 \mu\text{m}$, $10\text{-}500 \mu\text{m}$, $20\text{-}400 \mu\text{m}$, $50\text{-}300 \mu\text{m}$, $75\text{-}200 \mu\text{m}$, $100\text{-}150 \mu\text{m}$.

The thickness of the electrolyte may be adjusted based on the use of the electrolyte. In
10 particular, the thickness may be adjusted based on the conditions at the time of preparing the electrolyte.

The electrolyte may be adjusted at the time of forming the electrolyte to achieve specific mechanical properties. For example, the electrolyte may be adjusted to comprise a soft outer layer that can maintain contact with electrode materials while changing their
15 volume during cycling, while a firmer inner layer may facilitate mechanical handling of the electrolyte film, thereby ensuring optimal ionic conductivity when in use.

The electrolyte may be suitable for use in batteries, particularly solid-state batteries. According to second aspect, there is provided a solid-state battery comprising a cathode, an anode, and a solid-state electrolyte according to the first aspect.

20 The battery may be any suitable battery. The battery may be a solid-state lithium-ion battery. For example, the battery may be a rechargeable battery. In particular, the battery may be a rechargeable battery comprising Li metal or Li metal alloy. Even more in particular, the battery may be a Li-S battery.

The electrolyte may be suitable for use with different cathodes and anodes. For example,
25 the electrolyte may be suitable for use with sulphur-based cathodes, lithium-based cathodes, such as, but not limited to, LiFePO_4 , lithium cobalt oxide (LiCoO_2), lithium manganese oxides (LiMn_2O_4), lithium iron phosphate with or without Mn-doping ($\text{Li}_x\text{Fe}_{1-y}\text{Mn}_y\text{PO}_4$), or lithium nickel manganese cobalt aluminium oxides having general formula $\text{Li}_x\text{Ni}_a\text{Mn}_b\text{Co}_c\text{Al}_d\text{O}_2$, where $0 \leq a, b, c, d \leq 1$. The electrolyte may be suitable for use with
30 anodes comprising lithium titanate, lithium niobium titanate, or composites thereof with carbon phases.

The battery comprising the electrolyte may be a safer battery as it is an all-solid-state battery. In particular, the battery may withstand higher temperatures of up to about 80°C. The electrolyte when in use in a battery improves the cycle life of a battery as it enables better contact with volume-changing electrode materials due to the compressibility of the electrolyte. Further, the good wettability of the electrolyte as compared to the electrode materials leads to a large effective interface area between electrolyte and electrode phase, which substantially reduced the hazard of high local current densities as a leading cause for dendrite formation in brittle ceramic electrolytes.

A third aspect provides a method of preparing the solid-state electrolyte according to the first aspect, the method comprising:

- mixing a lithium ion conducting oxide with a polymer matrix to obtain a mixture;
- applying the mixture on a surface of a substrate; and
- curing the mixture coated on a surface of a substrate to form the electrolyte.

The method may be performed in a suitable environment. According to a particular aspect, the method may be performed in an inert environment. In particular, the method may be performed in the presence of an inert gas, such as, but not limited to, argon gas, nitrogen, or helium gas.

The mixing may comprise mixing the lithium ion conducting oxide and the polymer matrix in a suitable weight ratio based on the total weight of the mixture. For example, the mixing may comprise mixing 1-50 wt % lithium ion conducting oxide based on the total weight of the mixture. In particular, the mixing may comprise mixing 10-45 wt %, 15-40 wt %, 20-35 wt %, 25-30 wt % lithium ion conducting oxide based on the total weight of the mixture. The mixing may comprise mixing 40-99 wt % polymer matrix based on the total weight of the mixture. In particular, the mixing may comprise mixing 45-90 wt %, 50-85 wt %, 55-80 wt %, 60-75 wt %, 60-70 wt % polymer matrix based on the total weight of the mixture. According to a particular aspect, the weight ratio of the lithium ion conducting oxide to the polymer matrix comprised in the mixture may be 0.3:0.7 based on the total weight of the mixture.

The mixing may comprise stirring the mixture. The mixture may be stirred for a pre-determined period of time. For example, the mixture may be stirred for 1-12 hours. In

particular, the mixture may be stirred for 1-6 hours, 2-5 hours, 3-4 hours. Even more in particular, the mixture may be stirred for about 2-4 hours, particularly about 3 hours.

The applying may comprise applying the mixture by any suitable method. For example, the applying may comprise, but is not limited to, coating. In particular, the applying may
5 comprise coating, such as but not limited to, spin-coating, dip coating, spray coating, brush coating, electrospinning, or a combination thereof. Even more in particular, the applying may comprise spin-coating.

The applying may be under suitable conditions. The conditions under which the applying takes place may affect the eventual thickness of the formed electrolyte. According to a
10 particular aspect, the applying may comprise spin-coating the mixture on a surface of a substrate for a pre-determined period of time and at a suitable spin speed. For example, the pre-determined period of time may be about 60 seconds. For example, the spin-coating may be at a spin speed of 100-1000 rpm, particularly about 750 rpm.

The mixture may be coated on a surface of any suitable substrate. For example, the
15 substrate may be metallic or a non-metallic substrate. In particular, the substrate may comprise aluminium, copper, steel, glass, paper, bio-material which does not react with the electrolyte, or a combination thereof. Even more in particular, the substrate may be aluminium foil.

The curing may comprise curing the mixture under suitable conditions and for a pre-determined period. For example, the curing may comprise, but is not limited to ultraviolet
20 (UV) light curing, microwave curing, electron beam, laser curing, plasma curing, or a combination thereof. In particular, the curing may comprise UV light curing.

According to a particular aspect, the pre-determined period may be any suitable time depending on the polymerisation mechanism. In particular, the pre-determined period of
25 time may be ≤ 12 hours. For example, the curing may be for 5 seconds to 12 hours, 5 minutes to 10 hours, 30 minutes to 8 hours, 1-7 hours, 2-5 hours, 3-4 hours. Even more in particular, the curing may be for about 1-12 hours, particularly about 12 hours.

The method may further comprise removing the electrolyte from the surface of the substrate on which the electrolyte is formed. The removing may be by any suitable
30 method. For example, the removing may be by peeling, laser ablation, or a combination thereof. Accordingly, a free-standing solid electrolyte may be formed from the method.

The electrolyte formed may be in a suitable form. According to a particular aspect, the electrolyte formed may be in the form of a film. The formed film may have a suitable thickness. For example, the formed film may have a thickness of $\geq 1 \mu\text{m}$, particularly 5-50 μm . In particular, the thickness may be $\geq 10 \mu\text{m}$, 10-500 μm , 20-400 μm , 50-300 μm ,
5 75-200 μm , 100-150 μm . Even more in particular, the thickness may be 300-400 μm .

The method may further comprise forming the lithium ion conducting oxide prior to the mixing. The lithium ion conducting oxide may be formed by any suitable method. In particular, the method of forming lithium ion conducting oxide may comprise adding excess of the lithium ion source so that there is an excess of lithium ions in the reaction
10 mixture used for forming the lithium ion conducting oxide. The method may comprise grinding precursors for forming the lithium ion conducting oxide in a grinder, followed by step-wise annealing at a first temperature followed by annealing at a second temperature, and repeating the grinding and annealing, wherein the annealing is carried out at a third temperature. In particular, the second annealing temperature is higher than
15 the first annealing temperature, and the third annealing temperature is higher than the second annealing temperature. For example, the first annealing temperature may be about 500-600°C, the second annealing temperature may be about 800-950°C and the third annealing temperature may be about 1000-1200°C.

Annealing at each of the first temperature, second temperature and third temperature
20 may be carried out for a suitable period of time. For example, the first period of time, second period of time and the third period of time may be the same or different and may each be 1-20 hours, 2-18 hours, 5-15 hours, 8-12 hours, 9-10 hours. The method of forming the lithium ion conducting oxide described may enable preparation of the lithium ion conducting oxide in an overall shorter period of time as compared to prior art
25 methods. Further, the method of forming the lithium ion conducting oxide may be carried out outside a glove box.

According to a particular aspect, the method may further comprise forming LTPO as the lithium ion conducting oxide. The method of forming the LTPO may comprise a solid-state reaction of precursors, wherein the precursor comprises an excess of lithium
30 carbonate as the lithium ion source. The method may comprise grinding a mixture of Li_2CO_3 , Ta_2O_5 and $\text{NH}_4\text{H}_2\text{PO}_4$ for about 2 hours. The mixture may be annealed for 2 hours at a temperature of about 600°C, followed by annealing at a temperature of 900°C

for 8 hours. The annealed mixture may then be subjected to grinding again for about 1 hour and a subsequent annealing at 1050°C for 8 hours.

The method may further comprise forming the polymer matrix prior to the mixing. The method may comprise mixing a suitable amount of each of a monomer, initiator and plasticizer. A source of lithium ions may also be added during the mixing. Accordingly,
5 according to a particular aspect, the weight ratio of the monomer, plasticizer, lithium ion source and initiator may be 1:1.5:0.75:0.01.

The mixing to form the polymer matrix may be under suitable conditions. For example,
10 the mixing to form a polymer matrix may be in a dark environment if the monomer and initiator are photosensitive. The mixing to form a polymer matrix may be for a pre-determined period of time. The pre-determined period of time may be 1-20 hours, 2-18 hours, 5-15 hours, 8-12 hours, 10-11 hours. In particular, the pre-determined period of time may be 16 hours. The mixing may be at a suitable temperature. The temperature
15 may be 50-70°C, 55-65°C, 60-63°C. In particular, the temperature may be about 60°C.

The monomer may be any suitable monomer. The monomer may be, any monomer suitable for forming polymers with: non-polar heteroatom groups, such as but not limited to -O-; polar groups such as but not limited to -CF₃, -COOH, -C=O, -C≡N; charged groups such as but not limited to where Li⁺ acts as counter ion; and multi-type of ionic conductive
20 groups, as well as co-polymers and blends of these. For example, the monomer may be any monomer suitable for forming a polymer matrix which may comprise, but not limited to: polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), poly(ethyleneoxide) (PEO), poly(formaldehyde) (POM), poly(vinylpyrrolidone) (PVP), poly(ethylenecarbonate) (PEC), polypropylcarbonate (PPC), poly (vinylidene fluoride)
25 (PVDF), co-polymers and blends thereof. In particular, the monomer may be but not limited to: bisphenol A ethoxylate dimethacrylate (Bis-EMA).

The initiator may be a photoinitiator to initiate the polymerisation of the monomer. For example, the initiator may be, but not limited to, bis(diethylamino)benzophenone.

The plasticizer may be any suitable plasticizer. For example, the plasticizer may be, but
30 not limited to, nitrile-based plasticizers such as, but not limited to, succinonitrile, 4,7,10,13-tetraoxahexadecane-1,16-dinitrile (bCN-PEG4), bisphenol A ethoxylate dimethacrylate

or glycol ether-based plasticizers such as, but not limited to, tetraglyme. The amount of plasticizer added during the mixing affects the polymer matrix formed. For example, if the amount of plasticizer is too high, the flowability of the eventually formed electrolyte will be too high causing the electrolyte to behave like a liquid electrolyte. If the amount of plasticizer is too low, the flowability will be too low and the ionic conductivity of the electrolyte may be reduced.

The lithium ion source may be any suitable lithium ion source. In particular, the lithium ion source may be, but not limited to, lithium bistrifluoromethane sulfonimide. The amount of lithium ion source added during the mixing affects the polymer matrix formed. For example, if lithium salt ratio is increased beyond its solubility, lithium salt agglomeration may occur. However, if the ratio is too low, the eventual electrolyte may have a low ionic conductivity.

The method of preparing the solid-state electrolyte is a simple and low-cost method, which enables easy scale up as well as thickness of the electrolyte which can be tailored to specific applications. The electrolyte formed also has a high ionic conductivity. In particular, the electrolyte formed also comprises a polymer matrix which is soft which therefore ensures a good lasting contact with various electrode materials. This enhances the cycle life of the electrolyte, particularly when compared to solid state batteries which use brittle ceramic solid electrolytes only.

Having now generally described the invention, the same will be more readily understood through reference to the following example which is provided by way of illustration, and is not intended to be limiting.

Example

Preparation of LiTa_2PO_8

LiTa_2PO_8 was synthesized by solid-state reaction of Li_2CO_3 (99.9%, Aldrich), Ta_2O_5 (99.5%, Aldrich) and $\text{NH}_4\text{H}_2\text{PO}_4$ (99.99%, Aldrich). 10% excess Li_2CO_3 was added to compensate for lithium loss during high temperature processing. The precursors were ground in RM 200 (Retsch) mechanical grinder equipped with tungsten carbide pestle and mortar for 2 hours, followed by annealing at 600°C for 2 hours, 900°C for 8 hours, and ground again for 1 hour before a final annealing at 1050°C for 8 hours. This approach reduced the time of preparation of LiTa_2PO_8 compared to prior art methods.

Preparation polymer matrix and electrolyte

Bisphenol A ethoxylate dimethacrylate (Bis-EMA), succinonitrile, lithium bistrifluoromethane sulfonimide, Bis(diethylamino) benzophenone were mixed in the wt ratio of 1:1.5:0.75:0.01 using magnetic stirrer at 60°C for 16 hours. The samples were
5 kept in a dark environment throughout the mixing procedure as the precursors were photosensitive. The mixing resulted in the formation of a pale yellowish and transparent liquid.

In an argon-filled glove box, LiTa_2PO_8 was then mixed with the polymer matrix in the weight ratio of 0.3:0.7. The mixture was stirred for 3 hours. The final mixture was a white
10 viscous slurry. The obtained slurry was spin-coated onto an aluminum foil for 60 seconds at 750 rpm, followed by UV light curing for 12 hours. The formed electrolyte was white to yellow solid with ripples on the surface. The electrolyte was peeled off from the aluminum foil.

The overall thickness of the freestanding solid electrolyte polymer composite formed was
15 in the range of 0.3-0.4 mm. Thinner membranes down to about 10 μm may be fabricated by varying the spin coating rate and slurry viscosity and coating the slurry directly on electrode material supports.

Preparation of Li_2FePO_4 cathode

Li_2FePO_4 (LFP) was prepared using LFP, LTPO, ketjen black, polyvinylidene fluoride
20 binder in mass ratio of 40:32:8:20. The mixed ingredients were dissolved in 1-methyl-2-pyrrolidone (NMP) and stirred on a hot plate at 50°C, 200 rpm overnight. The slurry was coated onto aluminum foil using doctor blade. The coated electrode was dried at 80°C for 2 h followed by vacuum drying at 120°C overnight.

Preparation of S cathode

S:PVDF:conducting carbon was mixed in a weight ratio of 0.60:0.2:0.2. The mixture,
25 without PVDF, was first ground in a R-200 mortar equipped with tungsten carbide for 2 hours. PVDF and NMP was then added to the mixture, with stirring overnight at 300 rpm. The slurry was coated onto an aluminum foil using doctor blade. The wet coating thickness was about 400 μm . The coated electrode was dried at 80°C for 2 h followed
30 by vacuum drying at 90°C overnight.

Characterization

Both LiTa_2PO_8 and LiTa_2PO_8 polymer composite samples were characterized by X-ray powder diffractometry (Cu K) radiation, PANalytical X'Pert PRO diffractometer equipped with an X'Celerator fast linear detector. XRD data are collected in the 2θ range $10\text{--}80^\circ$ with a nominal scan rate of 160 s/step and a step size of 0.017° . SEM and EDX analysis of the LiTa_2PO_8 powder and composite polymer were recorded on a ZEISS Sigma 300.

Electrochemical characterization

Electrochemical impedance spectroscopy (EIS) data was obtained by Solartron SI1260 frequency response analyzer in combination with the 1296 dielectric interface. AC voltage was swept from 10 MHz to 1 Hz , with an amplitude of 0.1 V . Gold was coated on the surface of LiTa_2PO_8 pellet for EIS measurement. The polymer was tested using Swagelok, where stainless steel was provided as a blocking electrode for EIS measurement.

EIS for batteries was tested in the coin cell form. For the symmetric cell tests, two lithium foils were carefully attached to the polymer matrix. No pressure was applied during conductivity measurements or cell testing. Impedance measurement was done in the temperature range of 25 to 110°C .

Preparation of battery

CR2032 coin cells are assembled with lithium metal foil and LTPO composite and $20\text{ }\mu\text{l}$ of 1 M LiPF_6 in EC:EMC for Li-ion battery with LiFePO_4 cathode and $20\text{ }\mu\text{l}$ $1\text{ M (LiTFSI) + 0.1 M (LiNO}_3)$ in $1:1\text{ DME:DOL}$ for Li-S battery. The cells with LFP cathode in the voltage range of 2.0 V to 4.0 V and cells with S cathode in the voltage range of 1.7 to 2.8 V . All the fabrication was done in an Ar-gas filled glove box.

Results and discussions

XRD pattern of LTPO samples prepared at 1050°C is shown in Figure 1. All the peaks are explained by the LTPO phase, demonstrating that the sample is X-ray phase pure.

After solidifying, lithium-ion was chelated by electron-rich oxygen of ethylene oxide group of the polymer matrix. The lithium-ion are highly mobile and contributed to the ionic conductivity. In contrast, ceramics are prone to agglomerate thereby reducing surface

energy and form ceramic bridge. However, the polymer matrix occupies the vacancy between electrode and electrolyte.

Ionic conductivity:

The impedance of LTPO and LTPO composite was measured as a reference. The total conductivity of the LTPO pellet was $2.40 \times 10^{-4} \text{ S/cm}^{-1}$ and for LTPO composite it was $1.5 \times 10^{-3} \text{ S/cm}^{-1}$ at room temperature, as derived from Figure 2 which provides the Nyquist plot of the LTPO composite at room temperature. The increase of conductivity may be due to the additional LiTFSI and possible well connectivity among the ceramic particles. In the case of the polymer composite, the effect of grain boundary is removed, and total resistance was observed. The coordinated Li^+ migrated between or within polymer segments and chains as the lithium-oxygen (Li-O) bonds were broken/formed. At the same time, the polymer segments rearranged and moved to transport Li^+ over long distances. Thus, the increase of the amorphous region in polymer increased the movement of Li^+ in the electrolyte, indicating that the introduction of LTPO into the polymer matrix was effective.

Figure 3 provides the DSC curves of LTPO-polymer composite. The melting transition of polymer was 89.2°C after adding LTPO powders. This shows there is a strong interaction between the Lewis acid center of LTPO and TFSI^- , which leads to the separation of Li^+ from LiTFSI to release more Li^+ .

Performance of symmetric cells and batteries:

An important factor of all solid-state lithium-ion battery (ASSLB) is the interface stability of LTPO-composite/lithium metal. The lithium plating/stripping behaviour was measured at different current densities by assembling $\text{Li}||\text{LTPO-composite}||\text{Li}$ cells (0.1, 0.2 and 0.4 mA/cm^2). Figure 4 shows that $\text{Li}||\text{LTPO-composite}||\text{Li}$ cell presents a lower polarization voltage at all current densities and generates a more favourable electrolyte/lithium anode interface with no observed short-circuit in the current density range tested.

There was also a marked decrease in resistance for the symmetric cell over the first 10 h from 480Ω to close to 40Ω , as seen in Figure 5, suggesting an interfacial reaction between Li and LTPO-composite. No increase of resistance was observed more than 130 h.

A CR2032 semi-solid coin cell was assembled with lithium metal foil, LTPO-composite and 20 μL of 1M LiPF_4 in EC:EMC for better wettability and charge transfer and cathode composite coated on aluminum current collector. The coin cell was cycled between 2.0 V and 4.0 V with a constant current of 5×10^{-5} A. The voltage vs. capacity profiles of selected cycles is shown in Figure 6.

As shown in Figure 7, the discharge curve shows a 3.35 V plateau region. During the subsequent cycles charge- and discharge curves overlapped and only a minute hysteresis was observed. The overpotential was lower when compared with LTPO cells of prior art. The columbic efficiency reached nearly 99% until 110 cycles. The irreversible capacity loss (ICL) between the first-charge and discharge reaction was 20 mAh g^{-1} . After 110 cycles, the cell exhibited a capacity retention of 69%.

Li-S battery:

Cyclic voltammograms (CV) of Li-S are recorded with Li metal as the counter and reference electrode in the range 1.7 – 2.8 V at room temperature (RT) at the scan rate 0.001 mVs^{-1} for up to 5 cycles as shown in Figure 8. The compound shows first-cycle anodic peak at 2.42 V (vs. Li) whereas the corresponding cathodic peak was at 2.04 V and 2.29 V. From the second cycle onwards, the second anodic peak was at lower potential, 2.37 V. The two major reduction peaks around 2.3 V and 2.0 V, are related to the reduction of sulfur to high order LiPS (Li_2Sn , $4 \leq n < 8$), and the peak at the lower voltage is associated with the conversion of higher order LiPS to lower order LiPS (Li_2S_2 and Li_2S). The reactions were reversed in the anodic scan. The cathode displays cathodic and anodic peaks, demonstrating lithiation/delithiation kinetics. The increase of peak currents from cycle to cycle was due to the participation of more and more active material in the electrochemical process, which was also clearly reflected in the charge–discharge cycling curves as shown in Figure 9. The initial discharge specific capacity of the cells is 1050 mAh/g . The cell exhibited a capacity retention of 97% after 500 cycles.

The semi-solid coin cell assembled with lithium metal foil, LTPO-composite and 20 μL of 1 M (LiTFSI) + 0.1 M (LiNO_3) in 1:1 of DME:DOL for better wettability and charge transfer and cathode composite was coated on aluminum current collector. The coin cell was cycled between 1.7 V and 2.8 V with a constant current density of 5.36 mA/cm^2 (at C/2). The voltage vs. capacity profiles of selected cycles is shown in Figure 10. The discharge curve showed about 2 V plateau region. The irreversible capacity loss (ICL) between the

first-charge and discharge reaction was 103 mAh g^{-1} . The columbic efficiency reached nearly 96% after 500 cycles.

In conclusion, it can be seen that LTPO prepared using mortar grinding followed by annealing at 1050°C reduced the time of preparation of the electrolyte precursor material.

- 5 Subsequently, the prepared LTPO-composite electrolyte using UV curing was prepared by an easily scalable method. The electrolyte may be stable up to 89°C . The ionic conductivity observed was $1.5 \times 10^{-3} \text{ S/cm}$ at room temperature. The electrolyte may be compatible for both Li-ion and Li-S batteries. LiFePO_4 coin cell with polymer electrolytes exhibited capacity first discharge capacity of 157 mAh/g . Lithium sulfur battery using
- 10 polymer has shown an initial capacity of 1050 mAh/g .

Whilst the foregoing description has described exemplary embodiments, it will be understood by those skilled in the technology concerned that many variations may be made without departing from the present invention.

Claims

1. A solid-state electrolyte comprising a composite of a lithium ion conducting oxide and a polymer matrix, wherein the electrolyte has an ionic conductivity at 25°C of ≥ 1 mS/cm.
- 5 2. The electrolyte according to claim 1, wherein the electrolyte has an ionic conductivity at 25°C of ≥ 1.5 mS/cm.
3. The electrolyte according to claim 1 or 2, wherein the lithium ion conducting oxide
10 comprises at least one lithium ion polyanion oxide.
4. The electrolyte according to any preceding claim, wherein the lithium ion conducting oxide comprises $\text{Li}_x(\text{MO}_{6/2})_m(\text{TO}_{4/2})_t$ polyanion oxide, wherein:
M represents a cation M^{a+} , M being selected from the group consisting of: Ta, Nb, Ti,
15 Mo, W, V, Zr, Hf, Ge, Bi, Cr, Sb, In, Fe, Ga, and $3 \leq a \leq 6$;
T represents a cation T^{b+} , T being selected from the group consisting of: P, Si, Al, Ge, S, B, Pb, Mo, W, As, Se, Te, Mn, Sn, Zn, and $2 \leq b \leq 6$;
 $1 \leq m \leq 20$;
 $1 \leq t \leq 20$; and
20 x is $(6 - a) \times m + (4 - b) \times t$.
5. The electrolyte according to any preceding claim, wherein the lithium ion conducting oxide comprises LiTa_2PO_8 (LTPO).
- 25 6. The electrolyte according to any preceding claim, wherein the electrolyte comprises 1-50% lithium ion conducting oxide by weight based on the total weight of the electrolyte.
7. The electrolyte according to any preceding claim, wherein the electrolyte is in the
30 form of a film.
8. The electrolyte according to claim 7, wherein the film has a thickness of $\geq 1 \mu\text{m}$.

9. A solid-state battery comprising a cathode, an anode and a solid-state electrolyte according to any of the preceding claims.
10. The battery according to claim 9, wherein the battery is a Li-S battery.
- 5 11. A method of preparing the solid-state electrolyte according to any of claims 1 to 8, the method comprising:
- mixing a lithium ion conducting oxide with a polymer matrix to obtain a mixture;
 - 10 - applying the mixture on a surface of a substrate; and
 - curing the mixture coated on a surface of a substrate to form the electrolyte.
12. The method according to claim 11, wherein the mixing comprises mixing the
15 lithium ion conducting oxide in a weight ratio of 1-50 wt% based on the total weight of the mixture.
13. The method according to claim 11 or 12, wherein the curing comprises curing under ultraviolet (UV) light.
- 20 14. The method according to any of claims 11 to 13, wherein the curing is carried out for a period of ≤ 12 hours.
- 15 15. The method according to any of claims 11 to 14, wherein the method further comprises removing the electrolyte from the surface of the substrate on which the electrolyte is formed.
16. The method according to any of claims 11 to 15, wherein the method is performed in an inert environment.
- 30 17. The method according to any of claims 11 to 16, wherein the method further comprises forming the lithium ion conducting oxide prior to the mixing.
18. The method according to any of claims 11 to 17, wherein the method further
35 comprises forming the polymer matrix prior to the mixing.