A polymer electrolyte, method of forming, and method of upcycling the same

Technical Field

The present invention relates to a polymer electrolyte.

Background

Demand for energy storage is on an increasing trend. In commercially available lithium-ion batteries, liquid electrolytes are typically used, which present safety concerns from battery fires and explosions due to high flammability, possibility of leakage and formation of lithium dendrites. Thus, there has been growing interest in solid-state electrolytes.

However, current solid-state polymer electrolytes rely heavily on non-renewable petroleum resources, and are highly unsustainable once they reach the end-of-life. These are difficult to recycle and are disposed of in landfills or incinerators, which pollutes the environment.

There is therefore a need for an improved polymer electrolyte.

Summary of the invention

The present invention seeks to address these problems, and/or provides an improved polymer electrolyte.

According to a first aspect, there is provided a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts.

According to a particular aspect, the polyolefin backbone may comprise recycled polyolefin.

The graft copolymer may comprise a suitable amount of polyester. For example, the graft copolymer may comprise 20-95 wt. % of polyester based on total weight of the graft copolymer.

The polymer electrolyte may have any suitable weight ratio of polyester to alkali metal non-coordinating salt. For example, the weight ratio of polyester to alkali metal non-coordinating salt may be 1:1 to 20:1.

According to a particular aspect, the polyolefin may comprise polyethylene, polypropylene, polymethylpentene, copolymers, or mixtures and combinations thereof. The polyolefin may comprise high-density polyethylene (HDPE). The polyester may comprise polycaprolactone, polylactic acid, poly(hydroxyalkanoates), polylactones, poly(δ-valerolactone), copolymers, or mixtures and combinations thereof.

According to a particular aspect, the polyolefin may comprise high-density polyethylene (HDPE), and the polyester may comprise polycaprolactone, polylactic acid, copolymers, or mixtures and combinations thereof.

According to a particular aspect, the polymer electrolyte may be a solid polymer electrolyte (SPE). The SPE may have an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-4} S/cm at 20°C. The SPE may have an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-4} S/cm at 60°C.

According to a particular aspect, the polymer electrolyte may be a gel polymer electrolyte (GPE). The GPE may further comprise an ionic liquid. The ionic liquid comprised in the GPE may be in any suitable amount. For example, the ionic liquid comprised in the GPE may be 10-80 wt. % of the GPE. The GPE may have an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-2} at 20°C. The GPE may have an ionic conductivity of 1.0×10^{-6} to 1.0×10^{-1} at 60°C.

According to a particular aspect, the graft copolymer may not comprise any cross-links.

According to a second aspect, there is provided a method of forming a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts, the method comprising:

- mixing the alkali metal non-coordinating salt and the graft copolymer in a solvent to form a mixture;
- drying the mixture to form a paste; and
- hot pressing the paste to form the polymer electrolyte.

According to a particular aspect, the method may further comprise forming the graft copolymer prior to the mixing. The forming the graft copolymer may comprise polymerising monomer units of the polyester on a plurality of active sites on the polyolefin backbone, to form polyester grafts on the polyolefin backbone. The method may further comprise functionalising a polyolefin to form the plurality of active sites on the polyolefin backbone.

The polyolefin backbone may comprise recycled polyolefin.

According to a particular aspect, the mixing may further comprise adding an ionic liquid to the alkali metal non-coordinating salt and the graft copolymer.

According to a third aspect, there is provided a method of upcycling a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts, the method comprising:

- mixing the polymer electrolyte with a solution comprising nitric acid and a solvent to form a mixture;
- heating the mixture; and
- cooling the mixture to obtain C4-C11 dicarboxylic acids.

According to a particular aspect, the method may comprise adding an organocatalyst to the mixture prior to the heating.

The C4-C11 dicarboxylic acids may comprise > 20 wt. % of C4-C6 dicarboxylic acids.

Brief Description of the Drawings

In order that the invention may be fully understood and readily put into practical effect 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 a schematic representation of forming polymer electrolytes using graft copolymers, and thereafter valorising the end-of-life polymer electrolytes into industrially-relevant dicarboxylic acids;

Figure 2 shows the composition of the polymer electrolyte for energy storage in a cell according to one embodiment;

Figure 3 shows a reaction scheme of post-synthetic polyethylene (PE) functionalization and grafting of polycaprolactone (PCL) segments to form branched PE-PCL polymer electrolyte materials;

Figures 4(a) and (b) show the ^{1}H NMR spectra of PE-PCL copolymer, and polyethylene-polylactide (PE-PLA) copolymer, respectively;

Figure 5 shows the TGA measurements of the PE-PCL and PE-PLA copolymers;

Figure 6(a) shows the effect of higher LiTFSI loadings on ionic conductivities of PE-PCL SPEs at different temperatures; Figure 6(b) shows the effect of different quantities of LiTFSI and EMI-TFSI ionic liquid on PE-PCL GPEs at different temperatures;

Figure 7 shows the effect of temperature on ionic conductivity of (a) PE-PCL GPE film with [PCL]:[LiTFSI] = 6:1 (40wt% EMITFSI w.r.t. polymer), and (b) PE-PLA as GPE film with [PLA]:[LiTFSI]= 3:1, (40wt% EMITFSI w.r.t. polymer);

Figure 8(a) shows linear sweep voltammetry curves of PE-PCL GPEs electrolytes at scanning rate of 1 mV/s at 60°C (Li/PE-PCL GPE/stainless steel); Figure 8(b) shows cyclic voltammetry of Li/PE-PCL GPE/SS at a scan rate of 1 mV/s at 60°C; Figure 8(c) shows cyclic voltammetry of Li/PE-PCL GPE/LFP at a scan rate of 1 mV/s at 60°C; Figure 8(d) shows galvanostatic charge-discharge plots of the Li/PE-PCL GPE/LFP cell at 60°C (0.1C); Figure 8(e) shows cycling performance and coulombic efficiency of Li/PE-PCL GPE/LFP cell over 120 cycles (60°C, 0.1C); and Figure 8(f) shows rate performance of Li/PE-PCL GPE/LFP cell at various discharge rates at 60°C;

Figure 9 shows stacked ^{1}H NMR spectra (DMSO-d_6) showing the presence of succinic, glutaric and adipic acids from the oxidative upcycling of polymer electrolytes; and

Figure 10 shows the different quantities of succinic, glutaric and adipic acid formed from oxidative upcycling of PE-PCL, HDPE-OH and PCL, with or without Cl_4-NHPI catalyst, and with or without LiTFSI.

Detailed Description

As explained above, there is a need for an improved polymer electrolyte.

In general terms, the present invention provides a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts. In particular, the polyolefin backbone confers mechanical robustness for free-standing films to be formed, while the polyester grafts confers ionic conductivity in the presence of the alkali metal non-coordinating salt. Further, the polyolefin may be used post-synthesis, i.e., not from in-situ polymerisation of monomers. Thus, recycled polyolefins may be used. This reduces the amount of waste plastics disposed of, and keeps the material and its inherent properties within circular material loops, whilst simultaneously addressing an unmet need for more sustainable battery materials development.

In the present disclosure, the use of the singular includes the plural unless specifically stated otherwise. It should be noted that, as used in the specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly dictates otherwise. Further, the use of the term "including", "comprising", and "having" as well as other forms, such as "include", "comprise", "have" are not considered limiting.

According to a first aspect, there is provided a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts.

In the present disclosure, references to a graft copolymer refers to a segmented copolymer with a linear chain (or backbone) of one composite, and distributed branches (or grafts), of another composite.

The graft copolymer may comprise any suitable polyolefin backbone with any suitable polyester grafts. In particular, the polyolefin may be a thermoplastic polyolefin. For

example, the polyolefin may be polyethylene, polypropylene, polymethylpentene, copolymers, or mixtures and combinations thereof.

According to a particular aspect, the polyolefin may be polyethylene. The polyethylene may be ultra-high-molecular-weight polyethylene (UHMWPE), high-molecular-weight polyethylene (HMWPE), ultra-low-molecular-weight polyethylene (ULMWPE), high-density polyethylene (HDPE), medium-density polyethylene (MDPE), linear low-density polyethylene (LLDPE), low-density polyethylene (LDPE), very-low-density polyethylene (VLDPE), or mixtures and combinations thereof. In particular, the polyethylene may be high-density polyethylene (HDPE).

The polyester may be a thermoplastic polyester. For example, the polyester may be polycaprolactone, polylactic acid, poly(hydroxyalkanoates), polylactones, poly(δ-valerolactone), copolymers, or mixtures and combinations thereof.

In particular, the polyolefin may comprise high-density polyethylene (HDPE), and the polyester may comprise polycaprolactone, polylactic acid, copolymers, or mixtures and combinations thereof.

In the present disclosure, references to an alkali metal non-coordinating salt refers to a salt containing a non-coordinating anion, or weakly coordinating anion, which interacts weakly with an alkali metal cation. The alkali metal non-coordinating salt may be any suitable salt for use in polymer electrolytes. The alkali metal non-coordinating salt may comprise a lithium salt, sodium salt, potassium salt, or combinations thereof. According to a particular aspect, the alkali metal non-coordinating salt may be a lithium salt. For example, the alkali metal non-coordinating salt may be lithium bis(trifluoromethanesulfonyl)imide, lithium hexafluorophosphate, lithium perchlorate, or combinations thereof.

According to a particular aspect, the polyolefin backbone may comprise recycled polyolefin. In the present disclosure, references to a recycled polyolefin refers to a polyolefin which was treated as waste, and has undergone re-processing, mechanical, or chemical recycling, and is not directly derived from resins. The recycled polyolefin may have different properties from virgin polyolefin, for example, thermal, mechanical, and rheological properties, as a result of the re-processing and/or recycling. Thus, the present polymer electrolyte advantageously allows waste polyolefin to be converted

into more economically-valuable and high-demand products, and overcomes problems of low recycling rates due to inferior recycled products.

The graft copolymer may comprise a suitable amount of polyester. For example, the graft copolymer may comprise 20-95 wt. % of polyester based on total weight of the graft copolymer. In particular, the graft copolymer may comprise 25-90, 30-85, 35-80, 40-75, 45-70, 50-65, 55-60 wt. % of polyester based on total weight of the graft copolymer. Even more in particular, the graft copolymer may comprise 70-80 wt. % of polyester based on total weight of the graft copolymer.

The polymer electrolyte may have any suitable weight ratio of polyester to alkali metal non-coordinating salt. For example, the weight ratio of polyester to alkali metal non-coordinating salt may be 1:1 to 20:1. In particular, the weight ratio of polyester to alkali metal non-coordinating salt may be 2:1 to 19:1, 3:1 to 18:1, 4:1 to 17:1, 5:1 to 16:1, 6:1 to 15:1, 7:1 to 14:1, 8:1 to 13:1, 9:1 to 12:1, 10:1 to 11:1. Even more in particular, the weight ratio of polyester to alkali metal non-coordinating salt may be 3:1 to 12:1.

According to a particular aspect, the polymer electrolyte may be a solid polymer electrolyte (SPE).

The SPE may have an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-4} S/cm at 20°C. In particular, the SPE may have an ionic conductivity of 5.0×10^{-7} to 5.0×10^{-5}, 1.0×10^{-6} to 1.0×10^{-5} S/cm at 20°C. Even more in particular, the SPE may have an ionic conductivity of 1.0×10^{-7} to 2.0×10^{-5} S/cm at 20°C.

The SPE may have an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-4} S/cm at 60°C. In particular, the SPE may have an ionic conductivity of 5.0×10^{-7} to 5.0×10^{-5}, 1.0×10^{-6} to 1.0×10^{-5} S/cm at 60°C. Even more in particular, the SPE may have an ionic conductivity of 1.0×10^{-7} to 2.0×10^{-5} S/cm at 60°C.

According to a particular aspect, the polymer electrolyte may be a gel polymer electrolyte (GPE). The GPE may further comprise an ionic liquid. The ionic liquid may be any suitable ionic liquid for use in a GPE. For example, the ionic liquid may be a choline-based ionic liquid, an imidazolium-based ionic liquid, or mixtures and combinations thereof. In particular, the ionic liquid may be 1-ethyl-3-methylimidazolium

bis(trifluoromethylsulfonyl)imide (EMITFSI), 1-butyl-3-methylimidazolium chloride, or mixtures and combinations thereof.

The ionic liquid comprised in the GPE may be in any suitable amount. For example, the ionic liquid comprised in the GPE may be 10-80 wt. % of the GPE. In particular, the ionic liquid comprised in the GPE may be 15-75 wt. %, 20-70 wt. %, 25-65 wt. %, 30-60 wt. %, 35-55 wt. %, 40-50 wt. % of the GPE. Even more in particular, the ionic liquid comprised in the GPE may be 20-40 wt. % of the GPE.

The GPE may have an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-2} S/cm at 20°C. In particular, the GPE may have an ionic conductivity of 5.0×10^{-6} to 5.0×10^{-3}, 1.0×10^{-6} to 1.0×10^{-3}, 5.0×10^{-5} to 5.0×10^{-4}, 1.0×10^{-5} to 1.0×10^{-4}, 5.0×10^{-4} to 5.0×10^{-3} S/cm at 20°C. Even more in particular, the GPE may have an ionic conductivity of 1.0×10^{-5} to 1.0×10^{-3} S/cm at 20°C.

The GPE may have an ionic conductivity of 1.0×10^{-6} to 1.0×10^{-1} S/cm at 60°C. In particular, the GPE may have an ionic conductivity of 1.0×10^{-5} to 1.0×10^{-2}, 1.0×10^{-4} to 1.0×10^{-3} S/cm at 60°C. Even more in particular, the GPE may have an ionic conductivity of 1.0×10^{-5} to 1.0×10^{-3} S/cm at 60°C.

Thus, the polymer electrolytes advantageously have superior mechanical properties and ionic conductivity performance. The SPE and GPE also advantageously eliminates any risk of battery fires and explosions caused by electrolyte leakage.

According to a particular aspect, the graft copolymer may not comprise any cross-links.

According to a second aspect, there is provided a method of forming a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts, the method comprising:

- mixing the alkali metal non-coordinating salt and the graft copolymer in a solvent to form the mixture;
- drying the mixture to form a paste; and
- hot pressing the paste to form the polymer electrolyte.

The forming a mixture may comprise mixing the alkali metal non-coordinating salt with the graft copolymer dissolved in a solvent. The alkali metal non-coordinating salt and the graft copolymer may be as described above. The solvent may be any suitable solvent for dissolving the graft copolymer and dispersing the alkali metal non-coordinating salt. The solvent may be anhydrous. For example, the solvent may be 2-methyltetrahydrofuran (2-MeTHF), tetrahydrofuran (THF), ethyl acetate, or combinations or mixtures thereof.

The drying the mixture may comprise heating the mixture at any suitable temperature for any suitable period of time, such that a paste is formed. For example, the heating the mixture may be at 50-150 °C. In particular, the heating the mixture may be at 60-140 °C, 70-130 °C, 80-120 °C, 90-110 °C. Even more in particular, the heating the mixture may be at 60-100 °C. The heating the mixture may be for 1-72 hours. In particular, the heating the mixture may be for 5-70 hours, 10-65 hours, 15-60 hours, 20-55 hours, 25-50 hours, 30-45 hours, 35-40 hours. Even more in particular, the heating the mixture may be for 6-12 hours.

The hot pressing the paste may be induction heating, indirect resistance heating, or direct hot pressing. The hot pressing the paste to form the polymer electrolyte may be at any suitable predetermined temperature for any suitable predetermined period of time, at any suitable predetermined pressure, to form the polymer electrolyte. For example, the predetermined temperature may be 60-200 °C. In particular, the predetermined temperature may be 70-190 °C, 80-180 °C, 90-170 °C, 100-160 °C, 110-150 °C, 120-140 °C. Even more in particular, the predetermined temperature may be 90-110°C.

The predetermined period of time may be 10-120 minutes. In particular, the predetermined period of time may be 20-110 minutes, 30-100 minutes, 40-90 minutes, 50-80 minutes, 60-70 minutes. Even more in particular, the predetermined period of time may be 10-30 minutes.

The predetermined pressure may be 2-20 bar. In particular, the predetermined pressure may be 3-19 bar, 4-18 bar, 5-17 bar, 6-16 bar, 7-15 bar, 8-14 bar, 9-13 bar, 10-12 bar. Even more in particular, the predetermined pressure may be 3-8 bar.

According to a particular aspect, the method may further comprise forming the graft copolymer prior to the mixing. The forming the graft copolymer may be by any suitable method. For example, the forming the graft copolymer may be by a "grafting to" method which uses the backbone chain with functional groups distributed randomly along the chain, "grafting from" method in which a macromolecular backbone comprises active sites capable of initiating functionality for forming grafts, or "grafting through" method which uses a monomer of a lower molecular weight copolymerized with free radicals with an acrylate functionalized macromonomer.

The forming the graft copolymer may comprise polymerising monomer units of the polyester on a plurality of active sites on the polyolefin backbone, to form polyester grafts on the polyolefin backbone. The polyolefin may be used post-synthesis, i.e., not from in-situ polymerisation of monomers. Thus, the method may not comprise polymerising monomer units of the polyolefin. Accordingly, recycled polyolefins may be used in the method, therefore advantageously reducing the amount of waste plastics disposed of, while solving the problems caused by unsustainable materials used in prior art polymer electrolytes.

The polymerising may comprise adding any suitable catalyst to facilitate the polymerisation of the monomer units of the polyester. For example, the catalyst may comprise a metal catalyst, such as a Lewis acidic metal catalyst. In particular, the catalyst may comprise, but is not limited to, stannous octoate, indium(III) chloride, aluminum chloride, dibutyltin dilaureate, iron(III) chloride. The monomer units of the polyester may be ε-caprolactone, lactic acid, lactide, hydroxyalkanoate, lactone, or any combination thereof.

The polymerising may be at any suitable temperature for any suitable period of time, to allow polyester grafts to be formed on the polyolefin backbone. For example, the polymerising may be at 20-200 °C. In particular, the polymerising may be at 30-190 °C, 40-180 °C, 50-170 °C, 60-160 °C, 70-150 °C, 80-140 °C, 90-130 °C, 100-120 °C. Even more in particular, the polymerising may be at 80-120°C. The polymerising may be for 1-72 hours. In particular, the polymerising may be for 5-70 hours, 10-65 hours, 15-60 hours, 20-55 hours, 25-50 hours, 30-45 hours, 35-40 hours. Even more in particular, the polymerising may be for 12-24 hours.

In the present disclosure, references to active sites refer to locations on the backbone where chemical reactions take place and where grafts are eventually formed.

The active sites may be introduced by a post-polymerization reaction, and/or be an existing part of the backbone. For example, the active sites may be introduced by chemical modification of the backbone. The forming the graft copolymer may further comprise functionalising a polyolefin to form the plurality of active sites on the polyolefin backbone.

The functionalising may comprise any suitable functionalising of the polyolefin, including but not limited to, post-functionalization, so as to form active sites on the polyolefin backbone. For example, hydroxyl groups may be attached onto a pre-existing polyolefin backbone, i.e., hydroxyl functionalization, via aerobic oxidation of the polyolefin, followed by reduction. The functionalising may comprise adding an organocatalyst to a polyolefin in a suitable solvent to introduce carbonyl groups, and adding a reducing agent to convert the carbonyl groups to hydroxyl groups.

The organocatalyst may be any suitable organocatalyst, including but not limited to, organocatalysts comprising an N-OH group, with the exception of N-hydroxysuccinimide. For example, the organocatalyst may be N-hydroxyphthalimide (NHPI) and its derivatives. The NHPI derivatives may be halogen-substituted. For example, the NHPI derivatives may be Cl_4-NHPI, F_4-NHPI, Br_4-NHPI, 3,6-F_2-NHPI, 3-F-NHPI, 4F-NHPI, or any combination thereof. The solvent may be any suitable solvent. The solvent may be 1,2,4-trichlorobenzene (TCB), dichlorobenzene, toluene, tetrachlorobenzene, or mixtures and combinations thereof. The reducing agent may be sodium borohydride, sodium triacetoxyborohydride, sodium triethylborohydride, sodium cyanoborohydride, lithium borohydride, lithium tri-*sec*-butylborohydride, lithium aluminium hydride, or any combination thereof.

The polyolefin backbone may comprise recycled polyolefin. The recycled polyolefin may be as described above.

The polymer electrolyte formed from the method of the second aspect may be a solid polymer electrolyte (SPE).

According to a particular aspect, the polymer electrolyte formed from the method of the second aspect may be a gel polymer electrolyte (GPE). In this aspect, the mixing may further comprise adding an ionic liquid to the alkali metal non-coordinating salt and the graft copolymer. The ionic liquid may be any suitable ionic liquid for use in forming a GPE. For example, the ionic liquid may be a choline-based ionic liquid, an imidazolium-based ionic liquid, or mixtures and combinations thereof. In particular, the ionic liquid may be 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), 1-butyl-3-methylimidazolium chloride, or mixtures and combinations thereof.

The adding an ionic liquid may be in any suitable amount. For example, the adding may be such that the ionic liquid comprised in the GPE is 10-80 wt. % of the GPE. In particular, the adding may be such that the ionic liquid comprised in the GPE may be 15-75 wt. %, 20-70 wt. %, 25-65 wt. %, 30-60 wt. %, 35-55 wt. %, 40-50 wt. %. Even more in particular, the adding may be such that the ionic liquid comprised in the GPE may be 20-40 wt. %.

According to a third aspect, there is provided a method of upcycling a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts, the method comprising:

- mixing the polymer electrolyte with a solution comprising nitric acid and a solvent to form a mixture;
- heating the mixture; and
- cooling the mixture to obtain C4-C11 dicarboxylic acids.

In the present disclosure, references to upcycling refer to the process of converting waste into useful, valuable, and industrially relevant chemicals. The polymer electrolyte may be as described above.

The solution comprising nitric acid and a solvent may comprise any suitable solvent, which may be same as or different from the solvent used in forming a polymer electrolyte as described above. In a particular aspect, the solution comprising nitric acid and a solvent may comprise a suitable solvent different from the solvent used in

forming a polymer electrolyte as described above. For example, the solvent may be a green solvent. The green solvent may be characterised by its ease of recycling, ease of biodegradation, and/or low toxicity. The solvent may be acetic acid, γ-valerolactone, ethyl lactate, or any combination thereof. In particular, the solvent may be acetic acid. The amount of nitric acid and solvent may be in any suitable volume ratio with respect to the polymer electrolyte. For example, the volume ratio of nitric acid : solvent : polymer electrolyte may be 0.1:1:10 to 0.2:1:10. In particular, the volume ratio of nitric acid : solvent : polymer electrolyte may be 0.1:1.2:10 to 0.1:0.9:10, 0.1:0.7:10 to 0.1:0.8:10. Even more in particular, the volume ratio of nitric acid : solvent : polymer electrolyte may be 0.1:1:10.

The heating the mixture may be at any suitable temperature for any suitable period of time. For example, the heating the mixture may be at 60-200 °C. In particular, the heating the mixture may be at 70-190 °C, 80-180 °C, 90-170 °C, 100-160 °C, 110-150 °C, 120-140 °C. Even more in particular, the heating the mixture may be at 80-130 °C. The heating the mixture may be for 2-72 hours. In particular, the heating the mixture may be for 6-66 hours, 12-60 hours, 18-54 hours, 24-48 hours, 30-42 hours. Even more in particular, the heating the mixture may be for 12-24 hours.

The cooling the mixture may comprise cooling in ambient air.

According to a particular aspect, the method may comprise adding an organocatalyst to the mixture prior to the heating. The organocatalyst may be as described above.

The C4-C11 dicarboxylic acids may any mixture of dicarboxylic acids having chain lengths between 4 and 11 carbon atoms. The C4-C11 dicarboxylic acids may comprise > 20 wt. % of C4-C6 dicarboxylic acids. In particular, the C4-C11 dicarboxylic acids may comprise > 25 wt. %, > 30 wt. %, > 35 wt. %, > 40 wt. %, > 45 wt. %, > 50 wt. % of C4-C6 dicarboxylic acids. Even more in particular, the C4-C11 dicarboxylic acids may comprise > 50 wt. % of C4-C6 dicarboxylic acids. Thus, the polymer electrolyte may advantageously be broken down into industrially important short-chain dicarboxylic acids for further use in production of pharmaceuticals, adhesives, coatings, food additives, polymers, among many other applications. In this way, polymer electrolytes and/or battery cells containing the same which have reached their end-of-life can be easily upcycled into useful products, instead of being unsustainably disposed of.

The method of upcycling may not comprise separating the alkali metal non-coordinating salt from the graft copolymer prior to the mixing. Thus, the upcycling method is advantageously simple to perform.

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

Materials and methods

Synthesis of polyethylene-polycaprolactone (PE-PCL) copolymers

Figure 3 shows a scheme of post-synthetic polyethylene (PE) functionalization and grafting of polycaprolactone (PCL) segments to form branched PE-PCL polymer electrolyte materials.

(A) Organocatalytic oxidation of PE to install oxygenated groups

First, 5.09 g of HDPE (Mn ~7.7 kDa, Mw ~35 kDa, PDI = 4.55), and 1.36 g of N-hydroxytetrachlorophthalimide (Cl_4-NHPI) in 130 mL of 1,2,4-trichlorobenzene (TCB) solvent were added to a clean 500-mL round-bottomed flask equipped with a stir bar and condenser. The mixture was heated in an oil bath with constant stirring for 24 hours at 120 °C in air. Thereafter, the reaction mixture was precipitated slowly in a beaker of about 400 mL ethanol or methanol whilst stirring vigorously. Any residual TCB was removed from the polymer sample by breaking up any solid clumps and re-suspending the polymer in about 200 mL of ethanol or methanol, and left to stir overnight at room temperature before filtering. The precipitate was collected by suction filtration and dried in a vacuum oven at 60 °C.

(B) Synthesis of hydroxylated ROP precursor (HDPE-OH)

4.51 g of oxidised HDPE (from (A) above) was combined with 100 mL of toluene in a clean 500-mL round-bottomed flask equipped with a stir bar and condenser. The mixture was heated in an oil bath with constant stirring at about 100 °C until the polymer is fully dissolved. The solution was cooled to at least 60 °C before adding 70

mL tetrahydrofuran (THF), and 0.94 g sodium borohydride ($NaBH_4$) was then slowly added. The reaction mixture was heated at 90 °C with constant stirring overnight. The reaction mixture was then precipitated slowly in a beaker of about 400 mL ethanol or methanol whilst stirring vigorously. The precipitate was collected by suction filtration and dried in a vacuum oven at 60 °C.

(C)(i) Synthesis of PE-PCL branched copolymer

2.00 g HDPE-OH (from (B) above) was transferred to a clean and dry 200-mL Schlenk flask equipped with a stir bar. The flask was stoppered with a rubber septum. The sidearm of the flask to a Schlenk line was attached and the stopcock was carefully opened to vacuum for a few minutes. The flask with Ar or N_2 was backfilled. The evacuate-refill cycle was repeated at least twice more and the line left running under Ar or N_2 continuously. About 25 mL of dry toluene was added to the reaction flask.

2.2 mL stannous octoate [$Sn(oct)_2$] was dissolved in 5 mL of dry toluene in a glass vial, and transferred to the reaction flask. The vial was rinsed with 3 mL dry toluene and added into the same flask. Under constant stirring, 7.0 mL ε-caprolactone (CPL) was added to the reaction mixture, and the reaction mixture was heated in an oil bath at 110 °C with constant stirring for 42 hours.

The reaction mixture was cooled to 50 °C, and thereafter quenched with 100 mL acetone, and left to stir for 30 minutes. The mixture was poured into a beaker of about 200 mL methanol whilst stirring vigorously, to form a suspension.

The final polymer product was collected by suction filtration and dried under vacuum.

(C)(ii) Synthesis of polyethylene-polylactide (PE-PLA) copolymers

The procedure was similar to that in (C)(i), except that *L*-lactide (4.55 g) was added to the reaction mixture instead of ε-caprolactone.

<u>Fabrication of PE-PCL and PE-PLA polymer electrolyte films</u>

Varying amounts of the PE-based polymers, LiTFSI salt, and/or EMITFSI ionic liquid (for gel polymer electrolyte films) were added to anhydrous 2-methyltetrahydrofuran (2-

MeTHF) and stirred at 80°C until samples are fully dispersed/dissolved. The resultant solution was dried in a 80°C vacuum oven overnight to obtain a dry paste.

The various amounts of the PE-based polymers, LiTFSI salt, and/or EMITFSI ionic liquid are as shown in Table 1.

Polymer	Film composition (wt/wt. %)	Polymer / g	LiTFSI / g	EMITFSI / g	2-MeTHF / g
Solid polymer electrolytes (SPEs)					
PE-PCL	PCL: LiTFSI = 12:1	0.25	0.041	-	2.5
PE-PCL	PCL: LiTFSI = 6:1	0.25	0.082	-	2.5
PE-PLA	PLA: LiTFSI = 3:1	0.25	0.13	-	2.5
PCL	PCL: LiTFSI = 12:1	0.25	0.041	-	2.5
PCL	PCL: LiTFSI = 10:1	0.25	0.049	-	2.5
HDPE-OH	Same wt% loading of LiTFSI as entry 1	0.25	0.041	-	2.5
Gel polymer electrolytes (GPEs)					
PE-PCL	[PCL]:[LiTFSI]=12:1 22 wt% EMITFSI w.r.t. polymer	0.25	0.04	0.055	2.5
PE-PCL	[PCL]:[LiTFSI]=12:1 42 wt% EMITFSI w.r.t. polymer	0.25	0.04	0.105	2.5
PE-PCL	[PCL]:[LiTFSI]=6:1 40 wt% EMITFSI w.r.t. polymer	0.25	0.08	0.1	2.5
HDPE-OH	50 wt% LITFSI w.r.t. polymer; 20 wt% EMI-TFSI w.r.t. polymer	0.25	0.13	0.05	2.5
PE-PLA	[PLA]:[LiTFSI]=3:1 40 wt% EMITFSI w.r.t. polymer	0.25	0.13	0.1	2.5

Table 1: Amount of PE-based polymers, LiTFSI salt, and/or EMITFSI ionic liquid

The PE precursors, PE-PCL and PE-PLA paste were hot-pressed at different temperatures and pressures in 2 different steps. In particular, PE-precursors were kept at 110°C for 30 minutes to allow the paste to melt, followed by a pressure of 5 bar for 5 minutes. PE-PCL samples were preheated at 70°C for 10 minutes and a pressure of 20 bar was applied for 15 minutes. PE-PLA samples were preheated at 90°C for 10 minutes, followed by a pressure of 5 bar for 10 minutes.

The resultant films were then cooled rapidly using an air knife. All films were then dried under vacuum at 90°C for 2 days, followed by 80°C drying under argon overnight, to

obtain free-standing solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs) films.

Fabrication of Li ion cell with PE-PCL GPE film

PE-PCL GPE was used to fabricate Li-ion cells, using $LiFePO_4$ (LFP) as cathode and Li^0 as anode.

The Li/PE-PCL/LFP cells were assembled by sandwiching the gel polymer electrolyte between the Li anode and $LiFePO_4$ cathode using a CR2032 coin cell. The loading for active material in the electrode was 52 wt% ($\approx$ 2 mg/cm2) with 3 wt. % of carbon (Super C-65) and 45 wt. % PVDF binder and an ion conducting phase of PEO:LiTFSI (EO:Li ratio of 10:1). All electrodes were dried at 80°C under vacuum before cell assembly.

Upcycling of PE-PCL polymer electrolytes

The PE-PCL SPE (117.4 mg, comprising 84.6 wt% polymer and 15.4 wt% LiTFSI) and N-hydroxytetrachlorophthalimide (31.0 mg, 10 mol% w.r.t. average molecular weight of PE-PCL repeating unit, i.e., 96.7 g/mol) were weighed in a 10-mL Schlenk tube. Then, acetic acid (2 mL, 10 vol% of nitric acid) was added, followed by 70% nitric acid (0.2 mL, 3 equiv. w.r.t. average molecular weight of PE-PCL repeating unit).

The reaction mixture was stirred and heated to 125 °C for 24 hours in air. After the reaction had cooled to room temperature, diethyl ether (15 mL) was added to the crude reaction mixture before filtering to remove any unwanted solids. The filtrate was evaporated to dryness under reduced pressure to obtain a mixture of dicarboxylic acids.

The effect of the organocatalyst and LiTFSI on PE-PCL degradation was studied by performing two control experiments without these reagents respectively. The oxidative degradation process was also investigated on pure PCL (Mn 80 kDa) and the HDPE-OH precursor.

Characterisation

Nuclear magnetic resonance on oxidised PEs

The presence of functional groups in the oxidised PEs was identified by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) in TCE-d_2 at 80°C using a JEOL 500 MHz spectrometer (Tokyo, Japan).

Thermal characterization of copolymers

Thermogravimetric analysis (TGA) was conducted on the copolymers using TGA Q500 (TA Instruments) under N_2 with a flow rate of 60 mL/min. Each sample was heated from room temperature to 700 °C at a rate of 20 °C/min. Differential scanning calorimetry (DSC) was carried out using TA Instruments PDSC Q100 at a heating rate of 20 °C/min over a temperature range of -50 to 140 °C for PE-PLA and 190 °C for PE-PCL. Each sample was prepared and crimp sealed in an aluminium hermetic pan and lid inside a glovebox. The polymer melting temperature (T_m) was collected from the second cycle of heating.

Electrochemical measurements of electrolytes and cells

Ionic conductivity of the solid and gel polymer electrolyte films were characterized using a RHD piezo cell connected to an Autolab FR32 M frequency response analyzer.

Discs of 12mm diameter were cut and mounted onto the cell with symmetric stainless steel current collectors. Impedance spectra were obtained from 100 to 1 MHz at the temperature range of 20 to 80°C. The ionic conductivities were calculated according to the equation: $\sigma = \frac{l}{RA}$, where σ is the ionic conductivity at a certain temperature (K), l is the film thickness, R is the resistance, and A is the contact area (diameter = 8mm) of the electrodes.

Linear sweep voltammetry (LSV) was performed to determine the electrochemical stability of the gel polymer electrolyte, with a Li/PE-PCL/stainless steel coin cell. Cyclic voltammetry (CV) was performed at a scanning rate of 1 mV/s in the voltage range of -0.5 to 2 V for Li/PE-PCL GPE/SS cell (Figure S31A) and voltage range of 2 to 4 V for Li/PE-PCL GPE/LFP (Figure S31B) at 1 mV/s. All cells were assembled in an Ar-filled glovebox (O_2 and H_2O < 0.1 ppm).

The Li/PE-PCL/LFP cells were charged and discharged at constant current density from 0.1–2C in the voltage range of 2–4 V. All batteries were assembled in an Ar-filled

glovebox (O_2 and H_2O < 0.1 ppm). The galvanostatic measurements were carried out using a multichannel battery tester (Neware MHW-25) at 60°C. The coulombic efficiency (CE) was calculated using the following equation: CE = (discharge capacity)/(charge capacity) x 100%.

Analysis of upcycled products

Quantification of succinic, glutaric and adipic acids was done by ^{1}H NMR analysis in DMSO-d_6 with 1,2-dichloroethane (78.8 µL, 1 mmol) added as the internal standard.

LC-ESI-MS analysis of the dicarboxylic acids obtained from PE-PCL, PCL and PE-OH degradation was performed using an Agilent 6125 single quadrupole LC/MSD with Infinity II HPLC. Chromatographic separation was attempted using Hi-Plex H column (4.6 x 250 mm) coupled with its corresponding PL Hi-Plex H guard column (7.7 × 50 mm). The column temperature was maintained at 40 °C, and the flow rate and injection volume were set at 0.2 mL/min and 5 µL respectively. Mobile phase used for the analysis was 0.01% aqueous formic acid/acetonitrile = 80/20. The LCMS system was equipped with an ESI source operating in negative-ion detection mode.

Results and discussion

Nuclear magnetic resonance on oxidised PEs

As seen in Figures 4(a) and 4(b), the formation of PE-PCL and PE-PLA copolymers was evident from the appearance of the resonances at 4.86 ppm ($CDCl_3$) for PE-PCL and 4.88 ppm ($CDCl_3$) for PE-PLA, corresponding to Cα-H on the PE segment bonded directly to the grafted polyesters.

The proportion of PCL in PE-PCL was measured to be about 78 wt. %, whereas the proportion of PLA in PE-PLA was measured to be about 76 wt. %.

Thermal characterization of copolymers

From Figure 5, TGA characterization shows the presence of two decomposition peaks for PE-PCL at 323 °C and 481 °C. The former corresponds to the degradation of the PCL segment, whilst the latter results from thermal decomposition of the PE segment.

For PE-PLA, the first thermal degradation peak occurred at around 260°C, which corresponded to decomposition of the PLA segments.

It is notable that the degradation temperatures of the PE-PCL and PE-PLA polymers are much higher than typical operating temperatures of LiBs.

Electrochemical measurements of electrolytes and cells

As control samples, pure PCL films and pure oxidised HDPE-OH films were also formulated with LiTFSI salt using similar fabrication method as that for fabrication of PE-PCL and PE-PLA polymer electrolyte films. It was found that unlike the resulting SPE films of PE-PCL and PE-PLA which were free-standing and easy to handle for ionic conductivity determination, those produced using PCL alone with the same weight percentage loading of LiTFSI were found to be unsuitable for accurate electrochemical evaluation. Low percentage loadings of PCL: LiTFSI = 12:1 wt/wt% formed highly brittle films which disintegrated easily, whereas doubling the LiTFSI loading (PCL: LiTFSI = 6:1 wt/wt%) resulted in soft and tacky mixtures which could not be formed into films, as a result of the plasticising effect of LiTFSI.

Poor ionic conductivity was observed with the oxidised HDPE-OH precursor with an identical weight loading of LiTFSI, showing that the presence of PCL or PLA in the copolymer was essential for appreciable ionic conductivity.

Thus, both components of the copolymer contributed synergistically to achieve desired properties for polymer electrolytes, such as: (1) ease of processing into robust conductive films; and (2) practically-useful ionic conductivities.

Table 2 shows the ionic conductivities of the films as solid polymer electrolytes (SPEs) and gel polymer electrolytes (GPEs).

Polymer	Film composition (wt/wt. %)	Ionic conductivity at 20°C (S/cm)	Ionic conductivity at 60°C (S/cm)	E_a[a] / eV	R^2[b]
Performance as solid polymer electrolytes (SPEs)					
PE-PCL	PCL: LiTFSI = 12:1	2.0×10^{-6}	1.9×10^{-5}	0.49	0.999
PE-PCL	PCL: LiTFSI = 6:1	1.1×10^{-6}	1.6×10^{-5}	0.56	0.997
PE-PLA	PLA: LiTFSI = 3:1	$< 10^{-7}$	$< 10^{-7}$	-[c]	-[c]
PCL	PCL: LiTFSI = 12:1	-	-	-	-
PCL	PCL: LiTFSI = 10:1	-	-	-	-
HDPE-OH	Same wt% loading of LiTFSI as entry 1	$< 10^{-7}$	$< 10^{-7}$	-[c]	-[c]
Performance as gel polymer electrolytes (GPEs)					
PE-PCL	[PCL]:[LiTFSI]=12:1 22 wt% EMITFSI w.r.t. polymer	8.1×10^{-6}	6.0×10^{-5}	0.44	0.999
PE-PCL	[PCL]:[LiTFSI]=12:1 42 wt% EMITFSI w.r.t. polymer	4.7×10^{-5}	2.3×10^{-4}	0.35	0.994
PE-PCL	[PCL]:[LiTFSI]=6:1 40 wt% EMITFSI w.r.t. polymer	3.8×10^{-5}	1.8×10^{-4}	0.34	0.996
HDPE-OH	50 wt% LITFSI w.r.t. polymer; 20 wt% EMI-TFSI w.r.t. polymer	1.1×10^{-7}	2.4×10^{-7}	-[c]	-[c]
PE-PLA[d]	[PLA]:[LiTFSI]=3:1 40 wt% EMITFSI w.r.t. polymer	2.7×10^{-7}	1.2×10^{-5}	0.79	0.998

[a] Determined from the Arrhenius equation; [b] Goodness-of-fit determined from Figures 6(a) and 6(b); [c] Not determined due to low ionic conductivity observed; [d] See Figure 7(b) for temperature-dependence of ionic conductivity

Table 2: Electrochemical performance of copolymers as SPEs and GPEs

Figure 6(a) shows that the ionic conductivities of PE-PCL followed typical Arrhenius-like behaviour, with higher temperatures bringing about greater conductivity. The ionic conductivity of PE-PLA was found to be at least an order-of-magnitude lower than PE-PCL, even with a higher loading of LiTFSI.

As seen from Table 2, compared with SPEs, GPEs offer improved ionic conductivities by the incorporation of a liquid into the solid polymer matrix, without compromising on electrochemical stability and mechanical properties. The copolymers and LiTFSI were cast into free-standing, non-leaky GPE films containing varying quantities of EMI-TFSI ionic liquid. Free-standing homogeneous GPE films of PE-PCL containing LiTFSI and

EMI-TFSI were successfully fabricated. In contrast, a physical blend of PE and PCL (with similar molecular weight as that in the grafted PE-PCL copolymer films) which were not covalently grafted, together with LiTFSI and EMI-TFSI in the same ratios as that of the PE-PCL copolymer film, only formed a paste under identical fabrication conditions. Thus, the PE-PCL graft copolymer provided superior mechanical properties for film formation, even in the presence of the highly-plasticising EMI-TFSI ionic liquid. The presence of EMI-TFSI resulted in increased ionic conductivity of PE-PCL GPEs at identical loadings of LiTFSI, which were augmented at higher temperatures (Figure 6(b)).

Notably, with 22 wt% EMI-TFSI loading, similar E_a values (via the Arrhenius model) were obtained as that of the SPE, indicating that ionic conduction was likely to be still dominated by ion-hopping or polymer chain segmental motion akin to SPEs. However, further increasing the EMI-TFSI loading from 22 wt. % to 42 wt. % with respect to the polymer afforded more than an order-of-magnitude enhancement in ionic conductivity, with significant reduction in E_a. These suggested that a change in dominant mechanism of ionic conductivity occurred, likely involving conduction through the liquid phases percolating the PE-PCL polymer matrix through micropores in the presence of sufficient EMI-TFSI loading. However, doubling the LiTFSI loading did not result in further enhancement of ionic conductivity or E_a for ion conduction.

Linear Arrhenius-type behaviour (Figures 7(a) and 7(b)) for PE-PCL and PE-PLA GPE films was observed despite the temperature reaching beyond the first melting peak. This proved that the PE component which melts at 80°C, was able to provide mechanical support to prevent the polymers from melting completely.

Compared to PE-PCL, GPEs from the hydroxylated PE precursor and PE-PLA polymers showed poorer ionic conductivity. SEM imaging of the film cross-section showed smaller micropores compared to those of PE-PCL, possibly resulting in poor liquid phase percolation and thus, poor ionic conductivity observed.

The PE-PCL GPE was further investigated in Li-ion cells performance. Linear sweep voltammetry (LSV) (Li/PE-PCL GPE/stainless steel, 1 mV/s) showed the stability of the GPE within the potential window of up to 4.5 V versus Li/Li^+, which is well above the upper voltage limit of $LiFePO_4$ (LFP)-based cells (Figure 8(a)). There was a minor anodic peak observed initially in the first cycle, which thereafter disappeared as the cell

stabilized. The cyclic voltammetry (CV) plots showed the typical Li plating and stripping behaviour on the cathodic and anodic scans, with no other major peaks observed (Figure 8(b)). Similarly, the only peaks observed for the LFP-based cells correspond to oxidation and reduction peaks of Fe^{2+}/Fe^{3+}, further confirming the stability of the cell (Figure 8(c)).

Galvanostatic charge-discharge cycles performed between 2 and 4V at 0.1 C (60°C) showed flat charge and discharge profiles which indicated good electrochemical reversibility (Figure 8(d)).

According to the cycling performance, as shown in Figure 8(e), the Li/PE-PCL/LFP cell was able to maintain a very high Coulombic efficiency of 100% and initial discharge capacity of 160 mAh/g, close to the theoretical capacity of LFP at 170 mA h g^{-1}. The cell maintains its high capacity over 120 cycles, with capacity retention of > 80%.

The rate capability of the cell was investigated at different currents. Figure 8(f) shows that as cycling rate was increased from 0.1 to 0.3C, excellent retention of capacity (2% capacity fade) was observed. Although higher cycling rates resulted in greater decreases of capacity to 60 mA h g^{-1} at a high rate of 2C, initial capacity could be recovered when cycling rate returned to 0.1C.

Thus, it has been demonstrated that the copolymer GPE is electrochemically stable, and that no significant polymer degradation has occurred through repeated cycling.

Analysis of upcycled products

Through ESI-MS analysis, it was determined that a range of dicarboxylic acids possessing chain lengths between C4-C11 were formed during the oxidation process. Analysis of the product mixture by ^1H NMR showed succinic acid, glutaric acid, and adipic acid as the main products formed (Figure 9).

Figure 10 shows the amounts of each acid formed with different combinations of polymers and reagents, determined through quantitative ^1H NMR analysis with 1,2-dichloroethane as internal standard. By itself, catalysed oxidation of HDPE-OH afforded glutaric acid as the main product, with smaller quantities of succinic and adipic acid formed. This preference for C4 and C5 products can be expected as

depolymerisation likely occurs through a zip depolymerisation reaction involving cyclic transition states via backbiting mechanisms.

Under identical catalysed conditions, PCL produces mainly adipic acid, likely from tandem acid hydrolysis of the polyester followed by oxidation in situ. Under these conditions, shorter-chain succinic and adipic acid were also formed, possibly via decarboxylation to form terminal alkyl radicals which undergo further oxidation.

Similar product distributions were observed when the PCL oxidation reaction was repeated in the presence of 15 wt% LiTFSI. For the PE-PCL copolymers, the absence of Cl_4-NHPI in the reaction led to mainly adipic acid formation. However, addition of Cl_4-NHPI resulted in production of succinic and glutaric acid, reflective of the ability of the catalyst to enhance oxidation efficacy.

The importance of the Cl_4-NHPI catalyst was also seen where solids were seen in the catalyst-free reaction after 24 hours, which were shown by ^{1}H NMR analysis to be mainly unreacted PE fragments, indicating that only the PCL segment could be broken down in the absence of catalyst. In contrast, presence of the catalyst led to formation of clear homogeneous solutions, demonstrating that PE oxidative degradation has occurred.

Although addition of LiTFSI afforded slightly higher yields of glutaric and adipic acid, the differences are small despite the greater stoichiometric excess of LiTFSI compared to the catalyst, suggesting only minor influences on reactivity.

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 polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts.

2. The polymer electrolyte according to claim 1, wherein the polyolefin backbone comprises recycled polyolefin.

3. The polymer electrolyte according to claim 1 or 2, wherein the graft copolymer comprises 20-95 wt. % of polyester based on total weight of the graft copolymer.

4. The polymer electrolyte according to any preceding claim, wherein the weight ratio of polyester to alkali metal non-coordinating salt is 1:1 to 20:1.

5. The polymer electrolyte according to any preceding claim, wherein the polyolefin comprises polyethylene, polypropylene, polymethylpentene, copolymers, or mixtures and combinations thereof.

6. The polymer electrolyte according to any preceding claim, wherein the polyolefin comprises high-density polyethylene (HDPE).

7. The polymer electrolyte according to any preceding claim, wherein the polyester comprises polycaprolactone, polylactic acid, poly(hydroxyalkanoates), polylactones, poly(δ-valerolactone), copolymers, or mixtures and combinations thereof.

8. The polymer electrolyte according to any preceding claim, wherein the polyolefin comprises high-density polyethylene (HDPE), and wherein the polyester comprises polycaprolactone, polylactic acid, copolymers, or mixtures and combinations thereof.

9. The polymer electrolyte according to any of claims 1 to 8, wherein the polymer electrolyte is a solid polymer electrolyte (SPE).

10. The polymer electrolyte according to claim 9, wherein the SPE has an ionic conductivity of 1.0×10^{-7} to 1.0×10^{-4} S/cm at 20°C.

11. The polymer electrolyte according to claim 9, wherein the SPE has an ionic conductivity of 1.0 x 10^{-7} to 1.0 x 10^{-4} S/cm at 60°C.

12. The polymer electrolyte according to any of claims 1 to 8, wherein the polymer electrolyte is a gel polymer electrolyte (GPE).

13. The polymer electrolyte according to claim 12, wherein the GPE further comprises an ionic liquid.

14. The polymer electrolyte according to claim 13, wherein the ionic liquid comprised in the GPE is 10-80 wt. % of the GPE.

15. The polymer electrolyte according to any of claims 12 to 14, wherein the GPE has an ionic conductivity of 1.0 x 10^{-7} to 1.0 x 10^{-2} at 20°C.

16. The polymer electrolyte according to any of claims 12 to 14, wherein the GPE has an ionic conductivity of 1.0 x 10^{-6} to 1.0 x 10^{-1} at 60°C.

17. The polymer electrolyte according to any preceding claims, wherein the graft copolymer does not comprise any cross-links.

18. A method of forming a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts, the method comprising:

- mixing the alkali metal non-coordinating salt and the graft copolymer in a solvent to form a mixture;
- drying the mixture to form a paste; and
- hot pressing the paste to form the polymer electrolyte.

19. The method according to claim 18, the method further comprising forming the graft copolymer prior to the mixing.

20. The method according to claim 19, wherein the forming the graft copolymer comprises polymerising monomer units of the polyester on a plurality of active sites on the polyolefin backbone, to form polyester grafts on the polyolefin backbone.

21. The method according to claim 20, further comprising functionalising a polyolefin to form the plurality of active sites on the polyolefin backbone.

22. The method according to any of claims 18 to 21, wherein the polyolefin comprises recycled polyolefin.

23. The method according to any of claims 18 to 21, wherein the mixing further comprises adding an ionic liquid to the alkali metal non-coordinating salt and the graft copolymer.

24. A method of upcycling a polymer electrolyte comprising a graft copolymer and an alkali metal non-coordinating salt, wherein the graft copolymer comprises a polyolefin backbone and polyester grafts, the method comprising:

- mixing the polymer electrolyte with a solution comprising nitric acid and a solvent to form a mixture;
- heating the mixture; and
- cooling the mixture to obtain C4-C11 dicarboxylic acids.

25. The method according to claim 24, wherein the method comprises adding an organocatalyst to the mixture prior to the heating.

26. The method according to claim 24 or 25, wherein the C4-C11 dicarboxylic acids comprise > 20 wt. % of C4-C6 dicarboxylic acids.