



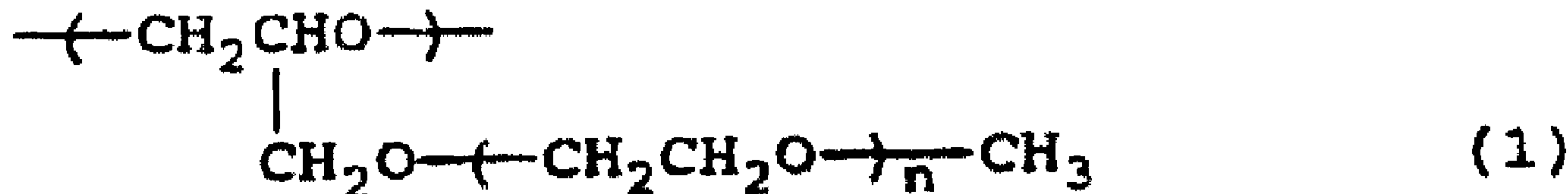
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(54) Titre : ELECTROLYTE SOLIDE A BASE DE POLYMERES
 (54) Title: POLYMER SOLID ELECTROLYTE



(57) **Abrégé/Abstract:**

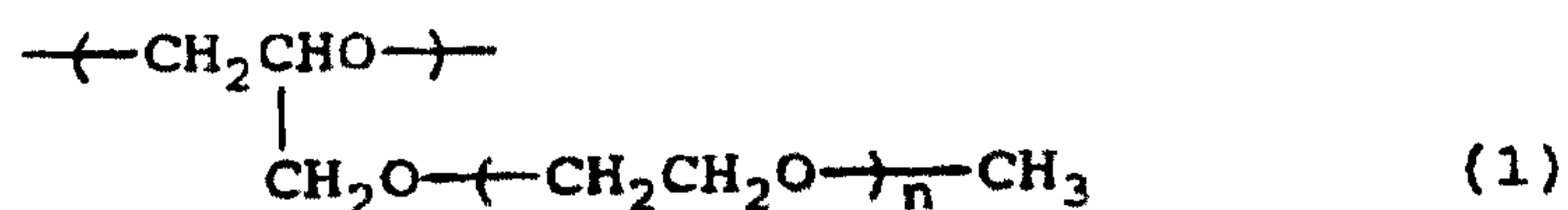
Disclosed is a polymer solid electrolyte which is superior to a conventional solid electrolyte in ion conductivity and also superior in processing characteristics, molding characteristics, mechanical strength and flexibility. The polymer solid electrolyte is produced by formulating a soluble electrolyte salt compound with a polyether copolymer having an oligooxyethylene side chain and an electrolyte salt compound which is soluble in the polyether copolymer, the polyether polymer being a solid random copolymer having a main chain structure consisting of 5 to 30 molar % of a structural unit of the following formula (1) and 95 to 70 molar % of a structural unit of the following formula (2), and the polyether polymer having a polymerization degree n of an oxyethylene unit of the side chain part of the formula (1) of 1 to 12, a number-average molecular weight of 100,000 to 2,000,000, a glass transition point measured by a differential scanning calorimeter (DSC) of not more than -60°C and heat of fusion of not more than 70 J/g. (see formula 1) (see formula 2)

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Abstract

Disclosed is a polymer solid electrolyte which is superior to a conventional solid electrolyte in ion conductivity and also superior in processing characteristics, molding characteristics, mechanical strength and flexibility. The polymer solid electrolyte is produced by formulating a soluble electrolyte salt compound with a polyether copolymer having an oligooxyethylene side chain and an electrolyte salt compound which is soluble in the polyether copolymer, the polyether polymer being a solid random copolymer having a main chain structure consisting of 5 to 30 molar % of a structural unit of the following formula (1) and 95 to 70 molar % of a structural unit of the following formula (2), and the polyether polymer having a polymerization degree n of an oxyethylene unit of the side chain part of the formula (1) of 1 to 12, a number-average molecular weight of 100,000 to 2,000,000, a glass transition point measured by a differential scanning calorimeter (DSC) of not more than -60°C and heat of fusion of not more than 70 J/g.



POLYMER SOLID ELECTROLYTE

FIELD OF THE INVENTION

The present invention relates to a polymer solid electrolyte. More particularly, it relates to a polymer solid electrolyte which is suitable as a material for an electrochemical device such as a battery, a capacitor, a sensor, etc.

BACKGROUND OF THE INVENTION

Conventionally the electrolyte constituting an electrochemical device such as a battery, capacitor, sensor, etc. has been used in the form of a solution or paste, to obtain the necessary ion conductivity. Often such devices become damaged, permitting leakage of liquid. In an attempt to solve this problem, a separator be impregnated with an electrolyte solution has been used. This has associated problems, such as a large minimum volume, limiting the possibility of ultra-miniaturization. As an alternative, a solid electrolyte, such as inorganic crystalline substances, inorganic glass, organic polymer substance, etc. have been proposed. Organic polymer substances are normally superior in processing characteristics and molding characteristics and the resulting solid electrolyte has flexibility and bending processing characteristics. The electrolyte may be shaped or fitted for many different applications. However, solid

electrolytes have inferior ion conductivity in comparison with other materials at present.

For example, the formulation of a specific alkaline metal salt into a mixture of an epichlorohydrin rubber and a low-molecular weight polyethylene glycol derivative and applying the resultant product to a polymer solid electrolyte is suggested in Japanese Laid-Open Patent Publication No. 2-235957 by the present applicant, but the conductivity is insufficient for practical use.

A polymer solid electrolyte obtained by crosslinking a polymer compound having an average-molecular weight of 1,000 to 20,000 described in Japanese Laid-Open Patent Publication Nos. 3-47833 and 4-68064 shows a comparatively good ion conductivity within a practical temperature, however further improvement is required.

A polyether copolymer having an oligooxyethylene side chain is described in Japanese Laid-Open Patent Publication Nos. 63-154736 and 63-241026 of the present applicant and European Patent Publication No. 434011 of the present applicant. These publications suggest the application of the polymer as a solid electrolyte or destaticizing material for plastic, but it is not described and suggested that those having a specific side chain length and a specific copolymer composition have excellent properties as an ion conductive solid electrolyte.

SUMMARY OF THE INVENTION

The present inventors have found that, by formulating a soluble electrolyte salt compound into a polyether copolymer having a specific composition ratio wherein oligoethylene glycol glycidyl ether is used in combination with ethylene oxide as copolymerization components, a solid electrolyte having an increased ion conductivity as compared with those using other epoxides (e.g. propylene oxide, epichlorohydrin, etc.) can be obtained.

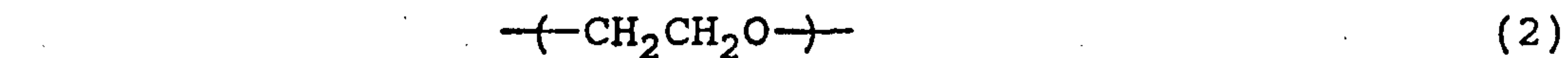
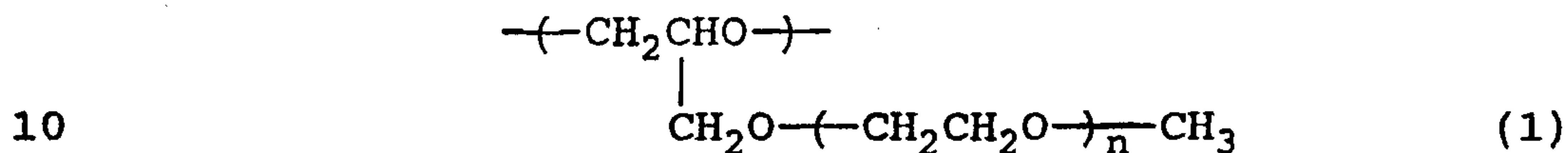
An object of the present invention is to provide a polymer solid electrolyte which is superior to a conventional solid electrolyte in ion conductivity and also superior in processing characteristics, molding characteristics, mechanical strength and flexibility.

Another object of the present invention provides a battery using the polymer solid electrolyte.

The present invention provides a polymer solid electrolyte comprising a polyether copolymer having an oligooxyethylene side chain and an electrolyte salt compound which is soluble in the polyether copolymer, the polyether polymer being a solid random copolymer having a main chain structure consisting of 5 to 30 molar % of a structural unit of the following formula (1) and 95 to 70 molar % of a structural unit of the following formula (2), and the polyether polymer having a polymerization degree n

of an oxyethylene unit of the side chain part of the
 formula (1) of 1 to 12, a number-average molecular weight
 of 100,000 to 2,000,000, a glass transition point measured by a
 differential scanning calorimeter (DSC) of not more than -60°C
 5 and a heat of fusion of not more than 70 J/g.

The present invention also provide a battery using the
 polymer solid electrolyte.



DETAILED DESCRIPTION OF THE INVENTION

The process for producing the polyether copolymer
 having an oligooxyethylene side chain (hereinafter referred
 to as a polyether copolymer) used in the present invention
 is described in the above-described Japanese Laid-Open
 20 Patent Publication No. 63-154736. That is, it is obtained
 by reacting the respective monomers corresponding to the
 above formulas (1) and (2) with stirring at a reaction
 temperature of 10 to 80°C in the presence or absence of a
 25 solvent, using a catalyst comprising mainly organic
 aluminum, a catalyst comprising mainly organic zinc, an
 organic tin-phosphate condensate catalyst, etc. as a
 catalyst for ring opening polymerization.

As the polyether copolymer used in the present
 30 invention, those whose molar ratio of the structural units

(1) and (2) is respectively 5 to 30 molar % (preferably from 10 to 30 molar %) and 95 to 70 molar % (preferably from 90 to 70 molar %) are suitable. When the molar ratio of the structural unit (2) exceeds 95 molar %, an increase in glass transition point and crystallization of the structural unit of the formula (2) arise. Therefore, it becomes impossible to maintain the glass transition temperature at not more than -60°C and the heat of fusion not more than 70 J/g. As a result, the ion conductivity of the solid electrolyte is drastically lowered. It is normally known that the ion conductivity is improved by lowering the crystallizability of ethylene oxide. It has been found that the effect of improving the ion conductivity is markedly large in the case of the polyether copolymer of the present invention. On the other hand, when the molar ratio of the structural unit of the formula (2) is less than 70 molar %, the softening temperature of the copolymer is decreased and it becomes difficult to obtain a solid electrolyte at room temperature (e.g. 20°C , etc.). The above glass transition temperature and heat of fusion are measured by a differential scanning calorimeter (DSC). In the present invention, those having a glass transition point of not more than -60°C (preferably not more than -65°C) and heat of fusion of not more than 70 J/g (preferably not more than 50 J/g) are suitable for use. The ion conductivity is lowered by those whose glass

transition point and heat of fusion exceed the above value.

In the present invention, the polymerization degree n of the oxyethylene unit of the side chain part of the formula (1) of the polyether copolymer is preferably from 1 to 12, more preferably 2 or 3. When it exceeds 12, the ion conductivity of the resulting solid electrolyte is lowered. The number-average molecular weight of the polyether copolymer is from 100,000 to 2,000,000, preferably 200,000 to 1,500,000, so as to obtain satisfactory processing characteristics, molding characteristics, mechanical strength and flexibility. When the number-average molecular weight is smaller than 100,000, the resulting electrolyte becomes liquid. On the other hand, when it exceeds 2,000,000, problems arise in processing characteristics and molding characteristics.

The electrolyte salt compound used in the present invention may be any one which is soluble in the polyether copolymer in the present invention, and the following compound is preferably used.

That is, it is a compound comprising 1) a cation selected from metal cation, ammonium ion, amidinium ion and guanidium ion and 2) an anion selected from chloride ion, bromide ion, iodide ion, perchlorate ion, thiocyanate ion, tetrafluoroborate ion, nitrate ion, AsF_6^- , PF_6^- ,

stearylsulfonate ion, octylsulfonate ion,
dodecylbenzenesulfonate ion, naphthalenesulfonate ion,
dodecyl naphthalenesulfonate ion, 7,7,8,8-tetracyano-p-
quinodimethane ion, $R_1SO_3^-$, $(R_1SO_2)(R_2SO_2)N^-$, (R_1SO_2)
5 $(R_2SO_2)(R_3SO_2)C^-$ and $(R_1SO_2)(R_2SO_2)YC^-$, wherein R_1 , R_2 , R_3
and Y is an electron attracting group. Preferably, R_1 , R_2
and R_3 independently indicate a perfluoroalkyl or
perfluoroaryl group having 1 to 6 carbon atoms, and Y is a
nitro group, a nitroso group, a carbonyl group, a carboxyl
10 group, a cyano group or a trialkylammonium group. R_1 , R_2
and R_3 may be the same or different.

As the metal cation, a cation of a transition metal
can be used. Preferably, a cation of a metal selected from
Mn, Fe, Co, Ni, Cu, Zn and Ag. Even when using a cation of
15 a metal selected from Li, Na, K, Rb, Cs, Mg, Ca and Ba,
excellent results can be obtained. It is possible to use
two or more sorts of the above compounds in combination as
the electrolyte salt compound. Among them, $LiPF_6$, $LiClO_4$ and
lithium bistrifluoromethanesulfonylimide (hereinafter
20 referred to as LiTFSI) are preferred in the case of a secondary
lithium battery because no substantial glass transition
point increase accompanies the addition of such electrolytes.

In the present invention, the amount of the soluble
electrolyte salt compound used for the total number of
25 ethylene oxide unit in the main chain and side chain of the
polyether copolymer, i.e. a ratio of the number of moles of

the electrolyte salt compound to the total number of moles of ethylene oxide is within the range from 0.0001 to 5, preferably from 0.001 to 0.5. When this value exceeds 5, the processing characteristics, molding characteristics as well as mechanical strength and flexibility of the resulting solid electrolyte are lowered, and the ion conductivity is also lowered.

The process for producing the polymer solid electrolyte of the present invention is not specifically limited, but the polymer solid electrolyte is produced by mechanically mixing the respective components, or dissolving them in a solvent and removing the solvent. As means for mechanically mixing, there can be optionally used various kneaders, open rolls, extruders, etc. When the polymer is produced using a solvent, various polar solvents such as tetrahydrofuran, acetone, acetonitrile, dimethylformamide, dimethyl sulfoxide, dioxane, methyl ethyl ketone, methyl isobutyl ketone, etc. may be used alone or in combination. The concentration of the solution is not specifically limited, but is preferably from 1 to 50% by weight. If necessary, the solid electrolyte may also be crosslinked. Examples of the crosslinking agent in case of crosslinking the copolymer include tolylene-2,4-diisocyanate, tolylene-2,6-diisocyanate, 4-4-diphenylmethane diisocyanate, hexamethylene diisocyanate, etc.

When using the polymer solid electrolyte of the present invention, it is possible to obtain a solid electrolyte in the shape of a large-surface area thin film, which has flexibility because of the polymer. For example, it is possible to produce a battery using the polymer electrolyte of the present invention. In this case, examples of materials which may be used for the positive electrode include lithium-manganese complex oxide, lithium cobaltate, vanadium pentoxide, polyacene, polypyrene, polyaniline, polyphenylene, polyphenylene sulfide, polyphenylene oxide, polypyrrole, polyfuran, polyazulene, etc. Examples of materials which may be used for the negative electrode include interlaminar compounds wherein lithium is occluded between layers of graphite or carbon, lithium metal, lithium-lead alloy, etc. One embodiment of the battery is shown in Example 8. It can also be used as a permeable membrane of an ion electrode of a cation such as alkaline metal ion, Cu ion, Ca ion, Mg ion etc. by making use of its high electric conductivity.

The polymer solid electrolyte of the present invention is superior in processing characteristics, molding characteristics, mechanical strength and flexibility, and the ion conductivity is remarkably improved. Accordingly, it is expected to be applied for solid battery, large-capacity condenser and display device (e.g. electronic equipment such as electrochromic display, etc.).

The following Examples and Comparative Examples further illustrate the present invention in detail but are not to be construed to limit the scope thereof.

Examples 1 to 4 and Comparative Examples 1 to 5

5 A polyether copolymer of Table 1 (1 g) (polyethylene oxide in the case of Comparative Example 3) was dissolved in tetrahydrofuran (20 ml), and then the resulting solution was mixed with a tetrahydrofuran solution of lithium perchloride so that a ratio of the number of moles of a
10 soluble electrolyte salt compound to the number of moles of an ethylene oxide becomes 0.005. This mixed solution was cast on a mold made of polytetrafluoroethylene, followed by sufficient drying to obtain a film.

The results of Examples and Comparative Examples are
15 shown in Table 1. In Table 1, the glass transition temperature and the heat of fusion were measured respectively in a nitrogen atmosphere under the condition of a temperature within the range of -100 to 80°C and a heating rate of 10°C/minute, using a differential scanning
20 calorimeter DSC8230B (manufactured by Rigaku Denki Co., Ltd.). The conductivity σ was measured using platinum as an electrode under the condition of a voltage of 0.5 V and a frequency within the range of 5 Hz to 1 MHz (A.C. method) according to a complex impedance calculation
25 method.

Example 5

A polyether copolymer (1 g) comprising 5 molar % of the structural unit of the formula (1) and 95 molar % of the structural unit of the formula (2) was dissolved in acetonitrile (20 ml), and then the resulting solution was mixed with an acetonitrile solution of LiTFSI so that the ratio of the number of moles of LiTFSI to the number of ethylene oxide units becomes 0.005. This mixed solution was cast on a mold made of polytetrafluoroethylene, followed by sufficient drying to obtain a film. According to the same manner as that described in Examples 1 to 4, characteristics of the film were measured. The conductivity of the solid electrolyte at 30°C was 4.0×10^{-4} S/cm.

It is apparent from a comparison with the Comparative Examples that the electrolyte of the present invention has excellent conductivity.

Example 6

A polyether copolymer (1 g) comprising 12 molar % of the structural unit of the formula (1) and 88 molar % of the structural unit of the formula (2) was dissolved in acetonitrile (20 ml), and then the resulting solution was mixed with an acetonitrile solution of LiTFSI so that the ratio of the number of moles of LiTFSI to the number of ethylene oxide units becomes 0.003. This mixed solution was cast on a mold made of polytetrafluoroethylene, followed by sufficient drying to obtain a film. According to the

same manner as that described in Examples 1 to 4,
characteristics of the film were measured.

Example 7

A film was obtained by the same method as the above
5 Example 6 except that the ratio of the number of moles of
LiTFSI to the number of ethylene oxide units was 0.05.
According to the same manner as that described in Examples
1 to 4, characteristics of the film were measured.

Example 8

10 A secondary battery was produced using the polymer
solid electrolyte obtained in Example 3 as the electrolyte,
a lithium metal foil as the negative electrode and lithium
cobaltate (LiCoO_2) as the positive electrode. The size of
the polymer solid electrolyte is 10 mm x 10 mm x 1 mm. The
15 size of the lithium foil is 10 mm x 10 mm x 0.1 mm.
Lithium cobaltate was prepared by mixing a predetermined
amount of lithium carbonate and cobalt carbonate powder and
calcining the mixture at 900°C for 5 hours. The resulting
lithium cobaltate was pulverized and a sufficient amount of
20 acetylene black is added thereto to improve the
conductivity and then subjected to press molding under a
pressure of 300 Kgw/cm² to form a positive electrode for
battery of 10 mm x 10 mm x 2 mm.

The polymer solid electrolyte obtained in Example 3
25 was interposed between the lithium metal foil and lithium
cobaltate plate and charging/discharging characteristics of
the battery were examined while applying a pressure of 10

Kgw/cm² so that the interface of the layers adheres closely.
The discharging current at the initial terminal voltage of
3.2 V was 0.4 mA/cm² and charging could be conducted at 0.3
mA/cm². In this Example, an extremely thin battery can be
5 produced and, therefore, the resulting battery is
lightweight and has a large capacity.

Table 1

	Example No.						
	1	2	3	4	5	6	7
Composition (molar %) of copolymer							
Ethylene oxide	79	90	95	93	95	88	88
Propylene oxide							
Epichlorohydrin							
Structural unit of the formula (1)	21	10	5	7	5	12	12
Polymerization degree of ethylene oxide of the side chain part (n)	2	2	2	8.5	2	3	3
Number-average molecular weight of copolymer	250,000	300,000	1,100,000	200,000	1,100,000	700,000	700,000
Glass transition temperature (°C)	-69	-67	-61	-67	-61	-68	-68
Heat of fusion (J/g)	17	48	67	58	67	44	44
Conductivity of solid electrolyte film σ (S/cm) 30°C	9.2×10^{-4}	8.9×10^{-4}	1.1×10^{-4}	6.3×10^{-4}	4.0×10^{-4}	7.8×10^{-4}	2.1×10^{-3}

Table 1 (continued)

	Comparative Example No				
	1	2	3	4	5
Composition (molar %) of copolymer					
Ethylene oxide	93	58	100		
Propylene oxide				89	
Epichlorohydrin					82
Structural unit of the formula (1)	7	42		11	18
Polymerization degree of ethylene oxide of the side chain part (n)	20	2		2	2
Number-average molecular weight of copolymer	250,000	200,000	200,000	250,000	250,000
Glass transition temperature (°C)	-63	-70	-59	-66	-31
Heat of fusion (J/g)	82	3	164	0	0
Conductivity of solid electrolyte film σ (S/cm) 30°C	9.2×10^{-5}	Pasty	1.4×10^{-6}	2.2×10^{-8}	1.8×10^{-9}

CLAIMS:

1. A polymer solid electrolyte comprising a polyether copolymer having an oligooxyethylene side chain and an electrolyte salt compound which is soluble in the polyether
 5 copolymer, the polyether copolymer being a solid random copolymer having a main chain structure consisting of 5 to 30 molar % of a structural unit of the following formula (1)



and 95 to 70 molar % of a structural unit of the following
 10 formula (2)



and the polyether copolymer having a polymerization degree n of an oxyethylene unit of the side chain part of the formula (1) of 1 to 12, a number-average molecular weight of 100,000 to
 15 2,000,000, a glass transition temperature measured by a differential scanning calorimeter (DSC) of not more than -60°C and a heat of fusion of not more than 70 J/g.

2. The polymer solid electrolyte according to claim 1,
 20 wherein the polyether copolymer comprising 10 to 30 molar % of the structural unit of the formula (1) and 90 to 70 molar % of the structural unit of the formula (2) is used.

3. The polymer solid electrolyte according to claim 1, wherein the polyether copolymer having a glass transition point of not more than -60°C and a heat of fusion of not more than about 50 J/g is used.

5

4. The polymer solid electrolyte according to claim 1, 2 or 3 wherein the electrolyte salt compound is a compound comprising a cation selected from metal cation, ammonium ion, amidinium ion and guanidium ion and an anion selected from chloride ion, bromide ion, iodide ion, perchlorate ion, thiocyanate ion, tetrafluoroborate ion, nitrate ion, AsF_6^- , PF_6^- , stearylsulfonate ion, octylsulfonate ion, dodecylbenzenesulfonate ion, naphthalenesulfonate ion, dodecyl-naphthalenesulfonate ion, 7,7,8,8-tetracyano-p-quinodimethane ion, R_1SO_3^- , $(\text{R}_1\text{SO}_2)(\text{R}_2\text{SO}_2)\text{N}^-$, $(\text{R}_1\text{SO}_2)(\text{R}_2\text{SO}_2)(\text{R}_3\text{SO}_2)\text{C}^-$ and $(\text{R}_1\text{SO}_2)(\text{R}_2\text{SO}_2)\text{YC}^-$, wherein R_1 , R_2 , R_3 and Y is an electron attracting group.

5. The polymer solid electrolyte according to claim 4, wherein R_1 , R_2 and R_3 independently indicate a perfluoroalkyl or perfluoroaryl group having 1 to 6 carbon atoms, and Y is a nitro group, a nitroso group, a carbonyl group, a carboxyl group or a cyano group.

6. The polymer solid electrolyte according to claim 4, wherein the metal cation is a cation of a metal selected from Li, Na, K, Rb, Cs, Mg, Ca and Ba.

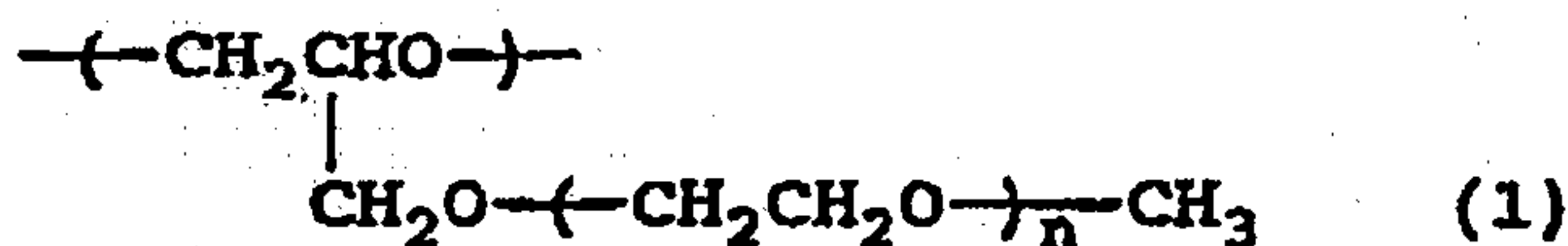
7. The polymer solid electrolyte according to claim 4,
wherein the metal cation is a cation of a transition metal.

8. The polymer solid electrolyte according to claim 4,
5 wherein the metal cation is a cation of a metal selected from Mn,
Fe, Co, Ni, Cu, Zn and Ag.

9. The polymer solid electrolyte according to claim 1,
wherein the polymer solid electrolyte has a formulation ratio
10 defined as the number of moles of the electrolyte salt compound
to the total number of moles of the ethylene oxide units in said
polyether copolymer, and said formulation ratio ranges from
0.0001 to 5.

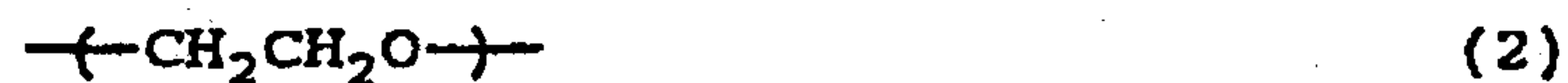
15 10. The polymer solid electrolyte according to any one of
claims 1 to 9, wherein the polyether copolymer has a number-
average molecular weight of 200,000 to 1,500,000.

11. A battery comprising a polymer solid electrolyte
20 comprising a polyether copolymer having an oligooxyethylene side
chain and an electrolyte salt compound which is soluble in the
polyether copolymer, wherein the polyether copolymer is a solid
random copolymer having a main chain structure consisting of 5 to
30 molar % of a structural unit of the following formula (1)



25

and 95 to 70 molar % of a structural unit of the following formula (2),



and the polyether copolymer having a polymerization degree n of
 5 an oxyethylene unit of the side chain part of the formula (1) of
 1 to 12, a number-average molecular weight of 100,000 to
 2,000,000, a glass transition temperature measured by a
 differential scanning calorimeter (DSC) of not more than -60°C
 and a heat of fusion of not more than 70 J/g.

10

12. The battery according to claim 11, wherein the
 electrolyte salt compound is selected from the group consisting
 of LiPF₆, LiClO₄ and LiTFSI.

15

13. The battery according to claim 11 or 12, wherein the
 polyether copolymer has a polymerization degree n of an
 oxyethylene unit of the side chain part of the formula (1) of 2
 or 3.

