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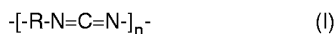
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(54) **BATTERY**

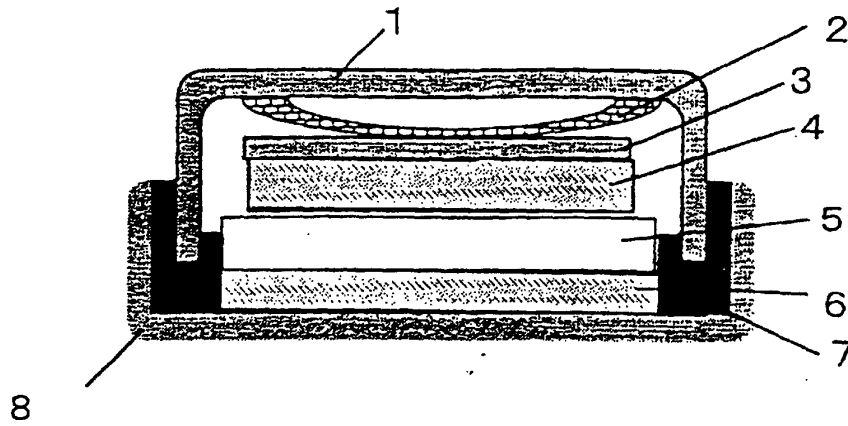
(57) A battery highly inhibited from suffering self-discharge.

The battery is characterized by containing a built-in polymer which has in the molecule a carbodiimide unit represented by the following formula (I):



(wherein R means an organic group and n means an integer of 1 to 10,000).

Fig. 1



Description

Technical Field

5 **[0001]** The present invention relates to a battery containing built-in polycarbodiimide. According to the invention, battery self-discharge is inhibited and the battery life is prolonged.

Background Art

10 **[0002]** Secondary batteries such as nickel-hydrogen cells and nickel-cadmium (Ni-Cd) cells are recently expected to be used as power sources for electric cars as well as small batteries for electrical/electronic appliances. Such a secondary battery is generally constituted of a positive electrode, a negative electrode, and a separator. Among these, the separator serves to prevent the cell from short-circuiting between the electrodes and enable ions to pass there-
 15 through, and is required to have hydrophilicity, chemical resistance, and mechanical strength. Conventionally known as a separator is a hydrophilic nonwoven fabric formed from a polyamide resin or the like. However, this separator has insufficient resistance to chemicals (alkalis and acids). Because of this, separators comprising polyolefin nonwoven fabrics which have undergone various treatments are also known. Specifically, separators obtained by subjecting a polyolefin-based nonwoven fabric to a hydrophilizing treatment, e.g., impregnation with a surfactant, plasma treatment, grafting treatment, sulfonation treatment, or the like, have been proposed (Unexamined Published Japanese Patent
 20 Applications Nos. 4-167355 and 11-238496, etc.).

[0003] Furthermore, since the polyamide-based nonwoven fabric has amide bonds, batteries employing this as a separator show a higher degree of self-discharge than batteries employing an electrochemically inert polyolefin nonwoven fabric and have poor battery properties. In contrast, batteries employing a separator obtained by subjecting a polyolefin-based nonwoven fabric to a specific treatment cannot be regarded as fully satisfactory in self-discharge
 25 characteristics, although superior in overall battery properties to batteries employing the polyamide-based separator.

[0004] Specifically, the separator obtained by treating a polyolefin-based nonwoven fabric with a surfactant shows effective hydrophilicity in the initial stage of use. However, when this separator is once immersed in water, taken out therefrom, dried, and reimmersed in water, then the hydrophilicity decreases considerably. In addition, this separator is unsatisfactory in self-discharge characteristics.

30 **[0005]** Furthermore, the polyolefin-based nonwoven fabric which has undergone a plasma treatment has hydrophilic groups bonded to the substrate surface by covalent bonding and hence retains sufficient wettability even when it is immersed in water, dried once, and reimmersed in water. Namely, it is wet-dry reversible. However, in the case where this nonwoven fabric is immersed in an aqueous alkali solution having a high concentration, it is not wetted by water when it is washed with water, dried, and reimmersed in water. It is presumed that the hydrophilic but weakly adherent,
 35 interfacial layer formed on the substrate surface by the plasma treatment was peeled off upon contact with the high-concentration aqueous alkali solution. This separator also is ineffective in greatly improving the inhibition of self-discharge.

[0006] In the case of the polyolefin-based nonwoven fabric which has undergone a grafting treatment, a water-soluble monomer is tenaciously bonded to a substrate by covalent bonding. However, the polyolefin treated by grafting with acrylic acid or methacrylic acid has the possibility of undergoing oxidative decomposition in a strongly oxidizing atmosphere because this polyolefin is of the carboxylic acid type. Consequently, this nonwoven fabric is used as a battery
 40 separator in limited applications.

[0007] Furthermore, the polyolefin-based nonwoven fabric which has undergone a sulfonation treatment has sulfo groups tenaciously bonded to the substrate by covalent bonding. Consequently, this nonwoven fabric retains long-
 45 lasting hydrophilicity and functions to inhibit a battery from suffering self-discharge. However, the treatment necessitates a post-washing step.

[0008] An object of the invention is to provide a battery which is sufficiently inhibited from suffering self-discharge and has excellent battery properties. The present inventors made extensive investigations on the self-discharge of batteries. As a result, it has unexpectedly been found that the self-discharge of a battery is considerably inhibited by
 50 causing polycarbodiimide to be present in the battery. The invention has thus been completed.

Disclosure of the Invention

55 **[0009]** The invention provides a battery containing a built-in polymer which has in the molecule a carbodiimide unit represented by the following formula (I):



(wherein R means an organic group and n means an integer of 1 to 10,000).

5 **[0010]** The battery of the invention can be inhibited from suffering self-discharge due to the built-in polycarbodiimide represented by general formula (I), which is disposed in any of various forms such as sheet, powder, and particles in or on an electrode or the separator or in other inner part of the battery.

[0011] The built-in polycarbodiimide may be disposed in any desired position within the battery. Furthermore, the battery is not particularly limited in steps for the production thereof. In the case where the polycarbodiimide is particulate or powdery, it may be placed in a bag made of a net or porous material having an opening diameter smaller than the particles, so as to prevent the polycarbodiimide from scattering. In the case where the polycarbodiimide is particulate or powdery, it may be present on the surface of or in an inner part of a porous separator substrate. It may have been deposited on the surface of the separator by coating. The polycarbodiimide may be present on the surface of or in an inner part of an electrode. It may also be present between the separator and an electrode. Incidentally, the polycarbodiimide may be crosslinked if desired.

Brief Description of the Drawings

[0012] [Fig. 1] A schematic sectional view illustrating one embodiment of the battery of the invention.

20 **[0013]** [Fig. 2] A schematic sectional view illustrating another embodiment of the battery of the invention.

[0014] [Fig. 3] A schematic sectional view illustrating still another embodiment of the battery of the invention.

[0015] [Fig. 4] A schematic sectional view illustrating a further embodiment of the battery of the invention.

Detailed Description of the Invention

25 **[0016]** The battery of the invention is not limited at all as long as it has built-in polycarbodiimide. The battery has a positive electrode, a negative electrode, and a separator interposed between the two electrodes. The other materials constituting the battery, including the electrolytic solution and battery case, may be conventionally known ones. Fig. 1 is a schematic sectional view of a battery (button type cell) of the invention. As shown in Fig. 1, a nickel wire gauze 2 and a nickel collector 3 are disposed in a cell inner case 1. Furthermore, a negative electrode 4, a separator 5 having polycarbodiimide, and a positive electrode 6 are superposed thereon and an outer cover 8 is attached through a packing 7. Figs. 2 to 4 are schematic sectional views illustrating other embodiments of the battery of the invention. In these embodiments, a polycarbodiimide film 9 is disposed in respective inner positions in the batteries. The battery according to the invention may be either a cylindrical cell containing electrodes and a separator which have been superposed and spirally wound or a prismatic cell comprising electrodes and a separator which have been superposed and packed in a case.

[0017] The separator or the porous sheet to be used as a separator substrate is not particularly limited in material. However, for use in applications where the separator is used in a strongly oxidizing or reducing atmosphere, e.g., like the separators for alkaline secondary batteries, the material thereof is preferably a polyolefin or the like having no specific functional groups.

40 **[0018]** Examples of the polyolefin to be used as the separator (or separator substrate) include homopolymers or copolymers of olefins such as ethylene, propylene, 1-butene, 4-methyl-1-pentene, and 1-hexene, blends of these polymers, and the like. Preferred of these are polypropylene and polyethylene. Especially preferred for use in a strongly oxidizing or reducing atmosphere as, e.g., the separator of an alkaline secondary battery or the like is ultrahigh-molecular polyethylene (hereinafter abbreviated as UHPE) having a weight average molecular weight of 1,000,000 or higher.

[0019] With respect to the form of the porous sheet, it is preferably a porous film or a nonwoven fabric. The porous sheet is not particularly limited in pore diameter or porosity.

50 (Application to Separator)

[0020] In the case where polycarbodiimide is applied to a separator, particles or a powder of the polycarbodiimide is disposed in pores of a porous sheet substrate. In producing such a separator, a sheet substrate is immersed in a dispersion of particles or a powder of the polycarbodiimide, or the dispersion is applied to the substrate, whereby the polycarbodiimide is infiltrated into pores of the porous substrate. Due to the incorporation of the particles or powder in pores of the separator, the separator has a substantially increased surface area and a reduced pore diameter, whereby the function of inhibiting self-discharge and liquid retentivity are improved. The dispersion is more preferably one in

which the dispersion medium is a polycarbodiimide solution. Upon drying, the solution forms a coating film on the surface of the fibers or particles constituting the separator, whereby not only the surface area of polycarbodiimide is increased but also the particles or powder is prevented from falling from the separator. The particles or powder of carbodiimide can be obtained by vacuum-drying a polycarbodiimide solution and optionally conducting pulverization.

5 **[0021]** Furthermore, use may be made of a separator obtained by coating at least part of the surface of a porous sheet substrate with polycarbodiimide. It is especially preferred to use as the sheet substrate a porous sheet obtained by sintering a powder of UHPE. The coating may be accomplished by immersing a sheet substrate in a polycarbodiimide solution and then evaporating the solvent by drying. If desired, the polycarbodiimide may be crosslinked.

10 **[0022]** In the case of using a porous sheet substrate consisting of a UHPE powder bonded to one another, this porous sheet usually preferably has a thickness of from 10 to 300 μm , a porosity of from 20 to 80%, and a pore diameter of from 1 to 500 μm . A UHPE porous sheet which can be used in the invention is obtained, for example, in the following manner. A UHPE powder is packed into a shape-retaining tool, and this shape-retaining tool is placed in a pressure vessel. The air present in the vessel is discharged. Subsequently, the powder is sintered in a water vapor atmosphere heated to a temperature not lower than the melting point of the UHPE and then cooled to thereby obtain a porous material in a block form. Thereafter, this porous material is sliced into sheets of a given thickness.

15 **[0023]** A polycarbodiimide-coated separator can be obtained by immersing a porous sheet substrate in a polycarbodiimide solution and then evaporating the solvent by drying. If desired, the polycarbodiimide may be crosslinked.

20 **[0024]** Furthermore, a porous sheet of polycarbodiimide which has been made porous by perforation, etching, or the like may be used as the separator. Examples of methods for producing this porous sheet include (i) a method in which a sheet is formed from a polycarbodiimide solution and this sheet is perforated with needles or a laser; and (ii) a method which comprises adding a particulate, powdery, or fibrous material to a polycarbodiimide solution, forming the mixture into a sheet, and then extracting the particulate, powdery, or fibrous material. It is also possible (iii) to obtain a porous sheet through chemical etching. Examples of methods for this chemical etching include the following method. A metal wire (copper wire, etc.) is coated with a polycarbodiimide solution, and this coated wire is tightly wound repeatedly on a core until the resultant structure comes to have a given diameter. Subsequently, the resulting structure is heated to a temperature not lower than the softening point (preferably not lower than the melting point) of the polycarbodiimide to thereby remove the solvent and simultaneously unite the loops of the coated metal wire. After cooling, this united tubular structure is sliced in a direction perpendicular to the metal wire to obtain a sheet having a given thickness. The metal wire is removed from this sheet with an etchant such as hydrochloric acid or sulfuric acid. In the case of using this chemical etching method, heating conditions usually include a temperature of from 140 to 200°C, a time period of from 0.5 to 5 hours, and an etchant concentration of from 0.1 to 10 mol/L. The porous separator thus obtained usually has a thickness of from 10 to 300 μm , a porosity of from 20 to 80%, and a pore diameter of from 1 to 500 μm .

25 **[0025]** For the purpose of improving initial wettability by an electrolytic solution, the porous sheet may be coated with a surfactant beforehand.

30 **[0026]** As the separator may also be used a sheet having a given thickness obtained by slicing either a porous sinter obtained by sintering a polycarbodiimide powder at a temperature not lower than the melting point thereof or a porous sinter obtained by sintering polycarbodiimide and polyolefin particles at a temperature not lower than the melting point of the polyolefin particles. As this polyolefin may be used the aforementioned polyolefins. Especially preferred is UHPE. Such a porous film in which UHPE has been blended can be produced, for example, in the following manner.

35 **[0027]** Particles of a polymer having carbodiimide units in the molecule are mixed with UHPE according to need, and this mixture is packed into a shape-retaining tool. The powder mixture packed is sintered by heating in a hot-air drying oven at a temperature not lower than the melting point of the UHPE. Alternatively, the shape-retaining tool is placed in a pressure vessel and, after the discharge of the air present in the vessel, the powder mixture is sintered in a water vapor atmosphere heated to a temperature not lower than the melting point of the UHPE. The resultant sintered powder mixture is cooled to obtain a porous sinter. Thereafter, this porous sinter is sliced into a given thickness, whereby a porous sheet can be produced.

40 **[0028]** Furthermore, a porous sheet produced by aggregating coated polymer particles obtained by forming a coating layer of polycarbodiimide on the surface of core particles made of a polyolefin resin or the like may be used as the separator. This porous sheet can be produced, for example, by forming a coating layer of the polycarbodiimide on the surface of core particles and sintering the coated polymer particles at a temperature not lower than the melting point of the core particles.

45 **[0029]** Incidentally, if n in formula (I) exceeds 10,000, the polycarbodiimide is insoluble in solvents and the desired polycarbodiimide-coated polymer particles cannot be obtained. From the standpoint of obtaining evenly coated polymer particles, n is preferably from 5 to 100, more preferably from 10 to 50.

50 **[0030]** For forming the core particles to be used for the coated polymer particles, either a thermoplastic or a thermosetting resin is used. Preferred are polyolefin resins such as polypropylene and polyethylene and fluororesins because these resins have excellent resistance to alkaline electrolytic solutions. Especially preferred is UHPE.

55 **[0031]** A coated polymer is produced in the following manner. When the polycarbodiimide is solid, it is dissolved in

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