Title: POLYMER ELECTROLYTE AND METHOD OF MANUFACTURING THE SAME

Abstract: Disclosed are a polymer electrolyte having a good mechanical strength and adhesiveness and a method of manufacturing thereof. First, a polyvinylidene fluoride-based polymer and an electrolytic solvent in which an electrolyte salt is dissolved are mixed in a mixing ratio of about 1:2-10 by weight. Then, a substantially homogenous electrolytic slurry is prepared by stirring and heating thus obtained mixture. After that, thus obtained electrolytic slurry is solidified to manufacture the polymer electrolyte. The polymer electrolyte has a good mechanical strength and illustrates a good adhesiveness to an electrode. A lithium secondary battery employing the polymer electrolyte illustrates a stable charge/discharge characteristic and a high capacitance.
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POLYMER ELECTROLYTE AND METHOD OF MANUFACTURING THE SAME

Technical Field

The present invention relates to a polymer electrolyte and a method of manufacturing the same and more particularly, to a polymer electrolyte having a good mechanical strength and a good adhesiveness to an electrode and a method of manufacturing the same.

Background Art

There has been a great deal of interest in developing better and more efficient methods for storing energy for applications such as cellular communication, satellites, portable computers and electric vehicles. In particular, great effort has been dedicated to the development of a lithium ion battery having a cathode including lithium, an anode including lithium or carbon and a non-aqueous electrolyte, because of its higher energy density than that of a lead storage battery or nickel-cadmium battery having an a non-aqueous electrolyte.

However, recently, the widely used lithium ion battery which has a satisfactory ionic conductivity uses a liquid electrolyte, however, the leakage of the liquid electrolyte occurs frequently. Moreover, any leakage in the cell lessens the performance and the safety of the battery. Accordingly, lithium ion batteries are packaged with an aluminum can and are provided with various protective devices, thereby enlarging the volume of the cell, and reducing the energy density to an undesirable degree. Furthermore, such a lithium ion battery is not applicable to a battery having a thickness of about 3mm or less.

In contrast, lithium ion polymer batteries which utilize a polymeric solid electrolyte instead of the liquid electrolyte, are free from problems of leakage. However, they tend to exhibit higher inner resistance compared to that of the liquid
electrolytes. This is attributed to the fact that the ionic conductivity of the solid electrolytes is often 5-100 times inferior to that of the liquid electrolytes.

In general, a lithium polymer secondary battery includes an anode, a polymer electrolyte and a cathode. The components are selected to satisfy various conditions of the secondary battery such as a lifetime, a capacity, a temperature characteristic, a stability, etc.

As for the components of the cathode applied to the lithium battery, lithium oxide complex compounds (for example, LiCoO₂, LiMn₂O₄, LiNiO₂, etc) can be used. The components have a laminated structure and lithium ions can be inserted between layers or separated from layers of the laminated structure. As for the components for the anode, carbon compounds such as graphite compounds or coke can be used. As for the examples of the graphite, mesocarbon microbeads (MCMB) and mesophase carbon fiber (MPCF) can be illustrated.

A polymer electrolyte which is widely used as a main component of the lithium battery, is free from the leakage problem. In addition, the battery using the polymer electrolyte has some advantages in manufacturing. However, the polymer electrolyte is required to have a good ionic conductivity, a thermal and electrochemical stability, a good mechanical strength and a good adhesiveness to the electrodes.

The polymer electrolytes which are currently used or under development include a main liquid-type organic solvent such as ethylene carbonate (EC) and propylene carbonate (PC), an auxiliary liquid-type organic solvent such as dimethyl carbonate (DMC), diethyl carbonate (DEC) and ethyl methyl carbonate (EMC). A lithium salt such as LiPF₆, LiAsF₆ and LiClO₄ can be mixed with the organic solvents to obtain an electrolyte. As for the polymer, polyvinylidene fluoride (PVdF), polyacrylate, polyethylene oxide, a mixture thereof, and the like can be used.

The polymer electrolyte including the polyvinylidene fluoride compounds has
a good mechanical strength and so is widely applied for the manufacture of a separator of a lithium secondary battery, a capacitor, a sensor, etc. However, the adhesiveness to the electrodes is not sufficient and so a pressing process using heat is required for the attachment of the polymer electrolyte to the electrode.

As a conventional method of manufacturing the PVdF-based polymer electrolyte, a strong volatile solvent such as THF, acetone, etc., PVdF and a weak volatile electrolytic solvent such as 1M LiPF₆ in EC/PC (1/1) are mixed with each other at about 60°C and thus obtained mixture is coated by a spin coating method. Then the coated layer is dried to mold. Otherwise, PVdF and the electrolytic solvent are mixed and then heated to about 100-130°C while applying a pressure to form a film (see U.S. Pat. No. 5,296,318).

However, the polymer electrolyte manufactured by the above-described method looses almost all the adhesiveness characteristics through implementing the drying process of THF or the forming process of the film by heating with a pressure. Therefore, when attaching the polymer electrolyte to an electrode, an attaching method with a heat is applied. In addition, THF should be completely dried because THF might dissolve PVdF as a binder of electrode which is commonly used for the manufacture of the lithium ion battery.

A method of using a plasticizer and inorganic filler has been suggested. By this method, THF or acetone as a solvent, non-volatile solvent such as propylene carbonate, dibutyl phthalate, ethylene carbonate, dimethyl carbonate, etc. as the plasticizer, and alumina or silica as the inorganic filler are mixed at about 50°C and thus obtained mixture is coated to manufacture a polymer electrolyte (see U.S. Pat. No. 5,418,091). The plasticizer in thus manufactured polymer electrolyte is replaced with an electrolytic solvent by extracting the plasticizer to manufacture a battery. Recently, these manufacturing methods prevail for forming the polymer batteries (see U.S. Pat. Nos. 5,460,904 and 5,587,257).
Besides, various methods of manufacturing PVdF-based polymer electrolyte have been disclosed. For example, one method is concerned with changing the amount of the inorganic filler (see U.S. Pat. No. 5,631,103), another method employs a volatile solvent which cannot be applied to a battery (see U.S. Pat. No. 5,900,183), further another method is devoted to studies on the change of the molecular weight of PVdF (see U.S. Pat. No. 5,962,168).

In another method, a first solvent which is strong volatile and dissolves PVdF well, such as acetone or THF and a second solvent which is weak volatile and is miscible with PVdF, such as DBP (dibutyl phthalate), are mixed as a plasticizer. Then, a filling material such as silica or alumina as an inorganic filler is added to the plasticizer and then, a film is formed by using thus obtained mixture. The film is dried to remove the volatile material. At this time, DBP is removed through an extraction to form pores at the place where DBP has been located to form an ion passageway, to heighten an ionic conductivity of the filling material such as silica (see U.S. Pat. No. 5,418,091) and to prevent a short of the battery during the attachment by means of heat.

However, according to the method, the complete removal of DBP is very difficult and if a small amount of DBP remains in the electrolyte, the ion transmission is not advantageous and the remaining DBP becomes an impurity. In particular, the extracting process of DBP requires a long period of time and complicated equipments to raise the manufacturing cost.

As described above, in the various conventional systems, the strength of the polymer film itself is very high, however, the electrode and the electrolyte could not attach spontaneously. Accordingly, the polymer film should be attached to the electrode through applying a heat. At this time, the polymer is liable to melt through the applied heat and this weakens the mechanical strength of the polymer and heightens the possibility of inducing a short. This might lessen the productivity and
yield. In addition, the melted polymer might block the surface of the electrode to disturb an impregnation of the electrolytic solution into the electrode.

**Disclosure of the Invention**

It is an object of the present invention considering the above-described problems, to provide a PVdF-based polymer electrolyte having a good mechanical strength and a good adhesiveness to an electrode.

Another object of the present invention is to provide an advantageous method of manufacturing the above-described polymer electrolyte.

Further another object of the present invention is to provide a lithium secondary battery having a stable charge/discharge characteristic and a high capacitance by employing the above-described polymer electrolyte.

To accomplish the object, there is provided in the present invention a polymer electrolyte manufactured by solidifying an electrolytic slurry obtained by mixing a polyvinylidene fluoride-based polymer and an electrolytic solvent in which an electrolytic salt is dissolved, in a mixing ratio of about 1:2-10 by weight.

Particularly, an amount of ethylene carbonate is in a range of about 20-80% by weight based on the total amount of the electrolytic solvent.

Another object of the present invention is accomplished by a method of manufacturing a polymer electrolyte as follows. First, a polyvinylidene fluoride-based polymer and an electrolytic solvent in which an electrolytic salt is dissolved are mixed, in a mixing ratio of about 1:2-10 by weight. Then, a substantially homogeneous electrolytic slurry is prepared by stirring and heating thus obtained mixture. Thus obtained electrolytic slurry is solidified to manufacture the polymer electrolyte.

Preferably, the electrolytic slurry is prepared by stirring the mixture at a temperature range of about 60-150°C for about 5 minutes – 2 hours. In addition, the viscosity of the electrolytic slurry is in a range of about 1,000-100,000 cps.
Further another object of the present invention is accomplished by a lithium polymer secondary battery comprising a cathode, an anode and a polymer electrolyte positioned between the cathode and anode. The polymer electrolyte is manufactured by solidifying an electrolytic slurry obtained by mixing a polyvinylidene fluoride-based polymer and an electrolytic solvent in which an electrolytic salt is dissolved, in a mixing ratio of about 1:2-10 by weight.

Particularly, the cathode is manufactured by mixing about 23-35% by weight of an active material, about 0.5-2% by weight of a conductive material, about 15-25% by weight of the electrolytic slurry and about 40-60% by weight of a solvent, and the anode is manufactured by mixing about 23-35% by weight of an active material, about 0-2% by weight of a conductive material, about 15-25% by weight of the electrolytic slurry and about 40-60% by weight of the solvent.

According to the present invention, the adhesiveness of the polymer electrolyte to the electrode can be obtained by using the PVdF-based polymer electrolyte and by controlling the mixing amount thereof with an electrolytic solvent. In addition, a gel-type polymer electrolyte can be manufactured by mixing the PVdF-based polymer with an electrolytic solvent containing a lithium salt, then stirring thus obtained mixture at room temperature and then heating the mixture according to the present invention.

**Brief Description of Drawings**

The above objects and advantages of the present invention will become more apparent by describing preferred embodiments in detail with reference to the attached drawings in which:

FIG. 1 is a schematic planar view of a lithium secondary battery of a unit cell type including a polymer electrolyte manufactured by a preferred embodiment of the present invention;

FIG. 2 is a schematic cross-sectional view of a lithium secondary battery of a
unit cell type including a polymer electrolyte manufactured by a preferred embodiment of the present invention;

FIG. 3 is a schematic cross-sectional view of a lithium secondary battery of an integrated cell type including a polymer electrolyte manufactured by a preferred embodiment of the present invention;

FIG. 4 is a charging/discharging voltage profile according to time when a lithium secondary battery manufactured by Example 1 is charged/discharged by 0.2C rate;

FIG. 5 is a discharge capacity according to cycles when a lithium secondary battery manufactured by Example 1 is charged/discharged by 1C rate;

FIG. 6 is a voltage profile when a lithium secondary battery manufactured by Example 1 is discharged by 0.2C rate at -10°C;

FIG. 7 is a voltage profile according to a discharge rate after charging a lithium secondary battery manufactured by Example 1 by 1C rate;

FIG. 8 is a discharge capacity according to cycles when a lithium secondary battery manufactured by Example 3 is charged/discharged by 1C rate; and

FIG. 9 is a graph representing discharge capacities according to cycles when lithium secondary batteries manufactured by Examples 1, 4-5 and Comparative Example 1 are charged/discharged by 1C rate.

**Best Mode for Carrying Out the Invention**

The present will be described in detail below.

A polymer electrolyte is positioned between a cathode and an anode to prevent a contact between the cathode and the anode and functions as an intermediate of an ion transmission. Therefore, the polymer electrolyte should have a good mechanical strength and a high ionic conductivity as an ion transmitting intermediate. In addition, the polymer electrolyte should make a homogeneous and stable interface with the cathode and anode.
PVdF-based polymer contains a large amount of an electrolytic solvent with a lithium salt and keeps a good mechanical strength. In addition, even the PVdF-based polymer could not attach to an electrode, an electrolyte manufactured from a mixture of the PVdF-based polymer with a plasticizer and a sufficient amount of an appropriate component of an electrolytic solvent illustrates a good adhesiveness to the electrode.

In the present invention, an electrolyte having a desired characteristic can be manufactured by mixing the PVdF-based polymer with an electrolytic solvent containing an electrolytic salt in an appropriate mixing ratio.

At this time, the preferred mixing ratio of the polymer with the electrolytic solvent including the electrolytic salt, is in the range of about 1:2-10 by weight. If the mixing ratio of the polymer with the electrolytic solvent is more than the given ratio, the mixing ratio of the electrolytic solvent becomes too low and the ionic conductivity of the electrolytic solvent is lowered and the adhesiveness between the electrode and the electrolyte is lowered even though the mechanical strength of the electrolyte is increased. In order to accomplish a sufficient adhesiveness of the electrolyte to the electrode, the amount of the electrolytic solvent contained in the polymer electrolyte should be sufficient. However, if the mixing ratio of the electrolytic solvent exceeds the given ratio, the mechanical strength of the electrolyte is lowered and a short cut might be formed when manufacturing a cell even though the ionic conductivity of the electrolyte might be increased. More preferred mixing ratio of the polymer with the electrolytic solvent is in a range of about 1:4-8 by weight.

In addition, the weight average molecular weight of the polyvinylidene fluoride-based polymer is in a range of about 50,000-1,000,000 and a polymer dispersion degree (a ratio of the weight average molecular weight with respect to the number average molecular weight) thereof is in a range of about 1-4. When a
copolymer of polyvinylidene fluoride and hexafluoro propane is used, a preferred amount of hexafluoro propane (HFP) is in a range of about 2-30% by weight based on the total amount of the copolymer. The weight average molecular weight of the PVdF-HFP copolymer is in the range of about 50,000-1,000,000 and a polymer dispersion degree thereof is in a range of about 1-4.

If the weight average molecular weight of the polymer is lower than 50,000, the mechanical strength of the polymer electrolyte is weak and thus the polymer electrolyte could not properly function as a separator. If the molecular weight of the polymer is higher then 1,000,000, the viscosity of the electrolytic slurry is too high and the manufacture of the polymer electrolyte film is not advantageous.

As for the electrolytic solvent used for the manufacture of the polymer electrolyte, ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), γ-butyrolactone (γ-BL), etc. may be mentioned. These can be used alone or in a mixture form.

The mixing ratio of EC is 20% by weight or more based on the total amount of the solvent in order to illustrate an ionic conductivity of about $10^{-3}$ S/cm or more at room temperature. If the mixing ratio of EC is less than 20% by weight, the used lithium salt could not be sufficiently dissociated and so the ionic conductivity of the electrolyte is largely reduced. In addition, the preferred mixing ratio of EC is 80% by weight or less based on the total amount of the solvent in order to illustrate a high ionic conductivity at a low temperature. Therefore, the preferred mixing amount of EC is in the range of about 20-80% by weight based on the total amount of the solvent. More preferably, the mixing amount of EC is in the range of about 30-60% by weight based on the total amount of the electrolytic solvent.

When the amount of EC is reduced, the affinity of PVdF to the electrolytic solvent increases and so the mechanical strength of the polymer electrolyte increases. However, the porosity of the electrolyte decreases and the impregnating ratio of the
electrolytic solvent through the electrolyte decreases. On the contrary, when the mixing amount of EC increases, the polymer electrolyte becomes somewhat brittle and the impregnating amount of the electrolytic solvent through the electrolyte increases.

In order to prevent the crystallization of EC having a high dielectric constant and to improve the characteristic of the polymer electrolyte at a low temperature, a plasticizer having a low viscosity such as EMC, DMC, DEC, etc. is mixed to manufacture the polymer electrolyte. The preferred mixing ratio of EMC, DMC or DEC is in the range of about 20-80% by weight based on the total amount of the electrolytic solvent. When the amount of the electrolytic solvent having a low viscosity is less than 20% by weight, the viscosity of the electrolytic solvent increases and the characteristic at a low temperature is largely decreased. When the amount of the above-described electrolytic solvent is greater than 80% by weight, the stability of thus manufactured battery at a high temperature is lowered because a large amount of a volatile solvent is included in the electrolytic solvent. In addition, the excessive amount of the electrolytic solvent in the polymer electrolyte volatilizes during the manufacture of the cell and the adhesive characteristic of the electrolyte to the electrode is easily eliminated.

In order to illustrate the characteristic at a low temperature while keeping the mechanical strength of the polymer electrolyte, the polymer electrolyte can be manufactured by mixing PC or γ-BL. At this time, the preferred amount of PC or γ-BL along with EC is 80% by weight or less based on the total amount of the solvent. When the amount exceeds 80% by weight, the viscosity of the electrolytic solvent increases and the ionic conductivity at a low temperature decreases.

In addition, the preferred amount of PC or γ-BL with respect to EC is 60% by weight or less. For the case of PC, when the amount of PC exceeds 60% by weight based on the amount of EC, a dissociation phenomenon is increased when
employing graphite for the manufacture of the anode. Considering this, the preferred amount of PC or γ-BL is in the range of about 5-40% by weight based on the total amount of the solvent.

As for the lithium salt, 0.5-2M of lithium perchlorate (LiClO₄), lithium trifluoromethane sulfonate (LiCF₃SO₃), lithium borofluoride (LiBF₄), lithium hexafluorophosphate (LiPF₆), lithium arsenic hexafluoride (LiAsF₆), or a mixture thereof is preferably used. When the concentration of the lithium salt is less than 0.5M, the ionic conductivity is lowered, and when the concentration of the lithium salt exceeds 2M, the viscosity of the electrolyte is largely increased and an over-voltage of concentration in the electrolyte increases. Accordingly, the preferred concentration of the lithium salt is in the above-described range.

When manufacturing the polymer electrolyte, about 2-50% by weight of silicon oxide (SiO₂), zeolite or aluminum oxide (Al₂O₃) can be added based on the polymer mixture after preparing the polymer mixture.

The method of manufacturing the polymer electrolyte using the polymer mixture obtained by mixing the above-described components will be described below...

First, the polymer and the electrolytic solvent containing the electrolytic salt, are mixed in a mixing ratio of about 1 : 2-10 at room temperature. Then, the mixture is heated to about 60-150°C to prepare a homogeneous solution of the polymer and the electrolyte. During the heating, the polymer is dissolved into the electrolytic solvent to increase the viscosity and when the viscosity becomes about 1,000-100,000 cps, the homogeneous solution is solidified by a method such as casting to manufacture a polymer electrolyte.

The mixing at the room temperature is an important process for the homogeneous mixing of the polymer with the solvent. When the mixing time at room temperature is too short, a large number of clusters of the polymer are formed
and a homogeneous mixture is difficult to be obtained during the heating and so thus obtained polymer electrolyte also becomes non-homogeneous. Accordingly, a stirring at room temperature should be implemented for a sufficient time. The stirring time depends on the amount of the components, the kind of the components, etc. and so could not be limited to a specific range.

After completing the stirring at a room temperature, the mixture is heated to prepare an electrolytic slurry. When the heating temperature is too low, the polymer is not dissolved and an electrolytic film is not formed. Even though the electrolytic film is formed, a local portion where a large amount of the polymer is congregated, also is formed and this portion functions as a barrier of the ion transmission to reduce the ionic conductivity. Meantime, when the polymer electrolytic slurry is prepared at a high temperature, the dissociation reaction of the polymer is carried out and the mechanical strength of the polymer electrolyte film is reduced. This problem might induce an electric short through a contact of the cathode and anode during the manufacture of a cell. Accordingly, the stirring is preferably implemented at an appropriate temperature range for an appropriate time. However, the range of the temperature and time could not be specifically defined. The heating time of the polymer electrolyte is dependent on the components of the polymer electrolyte. For example, when the amount of EC in the electrolyte is increased, the affinity of PVdF polymer to the electrolytic solvent is decreased and the heating time for the formation of the gel is somewhat increased. On the contrary, when the amount of EC is decreased, the solubility of the electrolytic solvent approaches to that of PVdF and the polymer electrolyte is manufactured within a short time. After repeating experiments by the present inventors while considering the above-described factors, the stirring is preferably implemented at about 60-150°C for about 10 minutes – 5 hours.
Thus manufactured polymer electrolyte composition can be applied in various fields such as for the manufacture of a lithium polymer secondary battery, a capacitor, a sensor, and the like.

The method of manufacturing a lithium polymer secondary battery using the polymer electrolyte manufactured by the present invention will be described in detail, below.

The polymer electrolytic slurry prepared through applying the heating condition described above, is coated on a substrate to form a polymer electrolyte film. As for the substrate, a molded film from which the polymer electrolyte can be easily separated and which has no reactivity, a cathode or an anode, etc. can be used. When the polymer electrolyte film is formed on the molded film, two electrolytic films are prepared on two molded films, respectively. Then, the electrolytic films are attached to both sides of one electrode. At this time, the polymer electrolyte has a sufficient mechanical strength to separate the cathode and the anode and a high ionic conductivity. In addition, the polymer electrolyte has a sufficient adhesiveness to accomplish a homogeneous adhesion to the electrode.

From thus manufactured structure of polymer electrolyte/anode/polymer electrolyte, the cathode is attached onto one of the polymer electrolyte to manufacture a unit cell. At this time, when polymer electrolyte/cathode/polymer electrolyte is manufactured, the anode might be attached onto one of the polymer electrolyte. Thus manufactured cell has a structure of polymer electrolyte/anode/polymer electrolyte/cathode and the remaining polymer electrolyte at the other side is eliminated when the unit cell is the target. Thus manufactured unit cell has a structure of cathode/polymer electrolyte/anode. When an integrated-type cell is the target, a number of the structure of polymer electrolyte/anode/polymer electrolyte/cathode will be integrated. After that, the polymer electrolyte at the outer side is eliminated to obtain the integrated-type cell.
Otherwise, the heated polymer electrolytic slurry can be directly coated onto the cathode or anode. At this time, the thickness of thus obtained polymer electrolyte is preferably in the range of about 20-100\um. The integrated-type cell is manufactured by the same order with that used when using the molded film. The polymer electrolyte is coated onto both sides of the electrode to obtain a structure of polymer electrolyte/anode (or cathode)/polymer electrolyte and a counter electrode is attached onto one side of the polymer electrolyte to manufacture a unit cell. An integrated-type cell is manufactured by repeating the unit cell. The polymer electrolyte has a good mechanical strength and a good adhesiveness to the electrode during the manufacture of the integrated-type cell. Schematic diagrams on the unit cell and the integrated-type cell are illustrated in FIGS. 1-3.

FIG. 1 is a schematic planar view of a lithium secondary battery of a unit cell type including a polymer electrolyte manufactured by a preferred embodiment of the present invention. FIG. 2 is a schematic cross-sectional view of a lithium secondary battery of a unit cell type including a polymer electrolyte manufactured by a preferred embodiment of the present invention. And FIG. 3 is a schematic cross-sectional view of a lithium secondary battery of an integrated cell type including a polymer electrolyte manufactured by a preferred embodiment of the present invention. In the drawings, reference numeral 1 represents an anode, 4 represents a polymer electrolyte, 6 represents a cathode, 8 represents a current collector of a cathode and 10 represents a current collector of an anode.

After completing the manufacture of the unit cell or the integrated-type cell, the cell is additionally impregnated with a liquid electrolyte. This liquid electrolyte penetrates into the electrode and the electrolyte to increase the ion transmission between the electrode and the electrolyte. Accordingly, the impregnation process of the liquid electrolyte is implemented to improve the discharge of a high rate and low temperature characteristic of the cell.
At this time, EC, PC, DEC, DMC, EMC, γ-BL or a mixture thereof can be used as the electrolytic solvent and LiClO₄, LiCF₃SO₃, LiBF₄, LiPF₆, LiAsF₆, etc. can be used as for the lithium salt. The solvent might be the same or different with that used for the manufacture of the polymer electrolytic slurry. At this time, the solvent should be selected considering the mechanical strength of the polymer electrolyte and the discharge capacity and high/low temperature characteristic of the cell.

Meantime, a lithium secondary battery can be manufactured by employing the polymer electrolyte obtained according to the present invention. Otherwise, the cathode and anode can be manufactured by adding the polymer electrolyte composition according to the present invention. At this time, a lithium polymer secondary battery is manufactured by the following method.

That is, a cathode can be manufactured by mixing about 70-95% by weight of an active material, about 2-8% by weight of a binder and about 4-12% by weight of a conductive material, and an anode can be manufactured by mixing about 70-95% by weight of an active material and about 5-30% by weight of a binder. A lithium secondary battery is manufactured by positioning the polymer electrolyte between thus manufactured cathode and anode.

Alternately, a cathode and an anode can be manufactured by adding the polymer electrolyte according to the present invention. At this time, the cathode is manufactured by mixing about 23-35% by weight of an active material, about 0.5-2% by weight of a conductive material, about 15-25% by weight of a polymer electrolytic slurry according to the present invention and about 40-60% by weight of a solvent such as N-methyl pyrrolidone (NMP), dimethyl acetamide (DMA), dimethyl formamide (DMF), etc. The anode is manufactured by mixing about 23-35% by weight of an active material, about 0-2% by weight of a conductive
material, about 15-25% by weight of a polymer electrolytic slurry according to the present invention and about 40-60% by weight of a solvent.

When lithium metal is used as for the anode, the anode is formed from a lithium thin film or a lithium powder. Then, the polymer electrolyte film according to the present invention is inserted between the cathode and the anode to form a bi-cell or a unit cell. At this time, when the polymer electrolyte composition of the present invention is used, an integrated-type cell of the unit cell or the bi-cell also can be manufactured.

After that, the cell is inserted into a case and the case is sealed by using a vacuum wrapper. After standing at about 70°C, the cell is charged by a constant current by 0.2C rate at room temperature and then is charged by a constant voltage of 4.2V after the cell voltage reaches to 4.2V until the current reaches to about 1/5 – 1/20 of the current during charging at the constant current. Next, the cell is discharged by 0.2C rate and this procedure is repeated by 2-5 times. At this time, degassing and resealing process should be additionally implemented when a gas is generated from the inner portion of the cell.

Preferred examples on the manufacture of the polymer electrolyte and the lithium secondary battery using the same according to the present invention will be described below. However, it should be understood that the present invention is not limited to the following examples.

Example 1

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 8g of a mixture solution of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1/0.8/0.5 by weight) in which 1M LiPF₆ was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 1 hour. Thus obtained polymer electrolytic slurry was
cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60 μm and the toughness was excellent. At this time, the ionic conductivity of the obtained polymer electrolyte was measured to be 1.8 x 10^{-3} S/cm. The ionic conductivity was measured by using an alternate current impedance method. In addition, the cast polymer electrolyte had a good mechanical strength and a good adhesiveness to the electrode.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/propylene carbonate/ethyl methyl carbonate (0.4/0.3/0.3 by weight) in which 1M LiPF_6 was dissolved, and was sealed under a vacuum.

Example 2

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 8g of a mixture solution of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (2/0.8/0.5 by weight) in which 1M LiPF_6 was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 2 hours. Thus obtained polymer electrolytic slurry was cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60 μm and the toughness was excellent. At this time, the ionic conductivity of the obtained polymer electrolyte was measured to be 1.6 x 10^{-3} S/cm. The ionic conductivity was measured by using an alternate current impedance method. In addition, the cast polymer electrolyte had a good mechanical strength and a good adhesiveness to the electrode.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/propylene carbonate/ethyl methyl carbonate
(0.4/0.3/0.3 by weight) in which 1M LiPF$_6$ was dissolved, and was sealed under a vacuum.

Example 3

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 8g of a mixture solution of ethylene carbonate/propylene carbonate/dimethyl carbonate/ethyl methyl carbonate (2/1/2/1 by weight) in which 1M LiPF$_6$ was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 1 hour. Thus obtained polymer electrolytic slurry was cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60μm and the toughness was excellent. At this time, the ionic conductivity of the obtained polymer electrolyte was measured to be 1.4 x 10$^{-3}$S/cm. The ionic conductivity was measured by using an alternate current impedance method. In addition, the cast polymer electrolyte had a good mechanical strength and a good adhesiveness to the electrode.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/propylene carbonate/ethyl methyl carbonate (0.4/0.3/0.3 by weight) in which 1M LiPF$_6$ was dissolved, and was sealed under a vacuum.

Example 4

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 8g of a mixture solution of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1/0.8/0.5 by weight) in which 1.5M LiPF$_6$ was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 1 hour. Thus obtained polymer electrolytic slurry was
cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60μm and the toughness was excellent. At this time, the ionic conductivity of the obtained polymer electrolyte was measured to be 1.5 x 10^{-3} S/cm. The ionic conductivity was measured by using an alternate current impedance method. In addition, the cast polymer electrolyte had a good mechanical strength and a good adhesiveness to the electrode.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/propylene carbonate/ethyl methyl carbonate (0.4/0.3/0.3 by weight) in which 1M LiPF₆ was dissolved, and was sealed under a vacuum.

Example 5

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 8g of a mixture solution of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1/0.8/0.5 by weight) in which 2M LiPF₆ was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 2 hours. Thus obtained polymer electrolytic slurry was cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60μm and the toughness was excellent. At this time, the ionic conductivity of the obtained polymer electrolyte was measured to be 1.4 x 10^{-3} S/cm. The ionic conductivity was measured by using an alternate current impedance method. In addition, the cast polymer electrolyte had a good mechanical strength and a good adhesiveness to the electrode.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/propylene carbonate/ethyl methyl carbonate
(0.4/0.3/0.3 by weight) in which 1M LiPF₆ was dissolved, and was sealed under a vacuum.

Comparative Example 1

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 8g of a mixture solution of ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (1/0.8/0.5 by weight) in which 3M LiPF₆ was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 1 hour. Thus obtained polymer electrolytic slurry was cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60μm and the toughness was excellent. At this time, the ionic conductivity of the obtained polymer electrolyte was measured to be 1.3 x 10⁻³S/cm. The ionic conductivity was measured by using an alternate current impedance method. In addition, the cast polymer electrolyte had a good mechanical strength and a good adhesiveness to the electrode.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/propylene carbonate/ethyl methyl carbonate (0.4/0.3/0.3 by weight) in which 1M LiPF₆ was dissolved, and was sealed under a vacuum.

Comparative Example 2

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 6g of a mixture solution of ethylene carbonate/dimethyl carbonate (2/8 by weight) in which 1M LiPF₆ was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130°C for about 1 hour. Thus obtained polymer electrolytic slurry was cast on a substrate by means of a doctor
blade method. The thickness of the cast polymer film was about 60 \( \mu \text{m} \) and the toughness was excellent. At this time, since thus obtained polymer electrolyte contains a large amount of volatile dimethyl carbonate, the electrolytic solvent volatilizes within a short time after the manufacture of the film. Therefore, the polymer electrolyte could not be attached to the electrode.

Comparative Example 3

1.0g of Kynar 2801 (manufactured by Atochem Inc.) as a PVdF-based copolymer and 6g of a mixture solution of propylene carbonate/dimethyl carbonate (3/2 by weight) in which 1M LiPF\(_6\) was dissolved, were mixed for a sufficient time at room temperature. Then, the mixture was stirred at 130\(^\circ\)C for about 1 hour. Thus obtained polymer electrolytic slurry was cast on a substrate by means of a doctor blade method. The thickness of the cast polymer film was about 60 \( \mu \text{m} \) and the toughness was excellent. At this time, the ionic conductivity of the polymer electrolyte was measured to be 1.6 \( \times \) 10\(^{-3}\) S/cm. The ionic conductivity was measured by using an alternate current impedance method.

A cell was manufactured by integrating a cathode, thus obtained polymer electrolyte and an anode. Then, the cell was additionally impregnated with a mixture solution of ethylene carbonate/dimethyl carbonate (1/1.5 by weight) in which 1M LiPF\(_6\) was dissolved, and was sealed under a vacuum. When graphite was used as for the manufacture of the anode, the dissociation of the anode was found.

The following tests were implemented for the cell manufactured by the above-described Examples. The result is described with reference to the attached drawings.

FIG. 4 is a charge/discharge voltage profile according to time when a lithium secondary battery manufactured by Example 1 is charged/discharged by 0.2C rate. It
is known from FIG. 4 that a general charge/discharge characteristic as a lithium secondary battery is illustrated when the cell is charged/discharged by 0.2C rate.

FIG. 5 is a discharge capacity according to cycles when a lithium secondary battery manufactured by Example 1 is charged/discharged by 1C rate. Before measuring the charge/discharge characteristic at 1C rate, the cell was activated by charging/discharging for 2 cycles or more by 0.2C rate. As shown in FIG. 5, the capacitance is reduced by about 15% of the initial capacitance through progressing 500 cycles and a stable cycle characteristic is obtainable.

FIG. 6 is a voltage profile when a lithium secondary battery manufactured by Example 1 is discharged by 0.2C rate at −10°C. Before discharging the cell at the low temperature, the cell was charged at room temperature by 0.2C rate, stored at −10°C for 1 hour and then discharged by 0.2C rate for the measurement. As shown in FIG. 6, the performance of the lithium polymer secondary battery including the PVdF-based polymer electrolyte at the low temperature is illustrated as 80% or more of the discharge capacity.

FIG. 7 is a voltage profile according to a discharge rate after charging a lithium secondary battery manufactured by Example 1 by 1C rate after activating the cell by 0.2C rate for 2 cycles or more. In FIG. 7, A represents a discharge curve at 0.2C rate, B represents a discharge curve at 0.5C rate, C represents a discharge curve at 1.0C rate and D represents a discharge curve at 2.0C rate.

In FIG. 7, when the discharge capacity at 0.2C is set to 100, the discharge capacity at 0.5C is measured to 98%, the discharge capacity at 1.0C is measured to 95% and the discharge capacity at 2.0C is measured to 88%. The mean voltage during discharging is illustrated as 3.8V at 0.2C rate, 3.75V at 0.5C rate, 3.66V at 1.0C rate and 3.5V at 2.0C rate. This characteristic according to the rate during discharging is similar to that of the lithium ion battery. Accordingly, it is confirmed
that the discharging characteristic of the PVdF-based polymer electrolyte at a high rate of discharge, is good.

FIG. 8 is a discharge capacity according to cycles when a lithium secondary battery manufactured by Example 3 is charged/discharged by 1C rate. From FIG. 8, it is known that the cell employing propylene carbonate in the solid polymer electrolyte, illustrates 85% or over discharge capacity when comparing with the initial capacity based on 500 cycles.

FIG. 9 is a graph representing discharge capacities according to cycles when lithium secondary batteries manufactured by Examples 1, 4-5 and Comparative Example 1 are charged/discharged by 1C rate. For each example, the concentration of the lithium salt is different.

In FIG. 9, E corresponds to a charge/discharge characteristic of a lithium polymer secondary battery including an electrolyte with a lithium salt of 1M concentration (Example 1), F corresponds to that of 1.5M concentration (Example 4), G corresponds to that of 2M concentration (Example 5) and H corresponds to that of 3M concentration (Comparative Example 1). When the concentration of the lithium salt is 1M, 1.5M and 2M, the charge/discharge characteristics of them are similar. Based on 450 cycles, the discharge capacity of the cell including 1M lithium salt is 90% of the initial capacity, that of the cell including 1.5M lithium salt is 88% and that of the cell including 2.0M lithium salt is 87%. Accordingly, the cycle characteristic is somewhat reduced while the concentration of the lithium salt is increased. However, the difference is not significant.

When the concentration of the lithium salt is 3M, the cycle characteristic is largely reduced. Accordingly, it is known that the resistance due to the concentration of the lithium salt in the polymer electrolyte is largely increased when the concentration of the lithium salt exceeds 2M.
As described above, the polymer electrolyte according to the present invention has a good mechanical strength and a good adhesiveness to the electrode and can be advantageously attached to the electrode without applying any other means.

In addition, the leakage and the evaporation of the electrolytic solvent from the polymer electrolyte can be minimized and a cell having a stable charge/discharge characteristic can be accomplished. Further, the cell illustrates a high capacitance.

While the present invention is described in detail referring to the attached embodiments, various modifications, alternate constructions and equivalents may be employed without departing from the true spirit and scope of the present invention.
CLAIMS

1. A polymer electrolyte manufactured by solidifying an electrolytic slurry obtained by mixing a polyvinylidene fluoride-based polymer and an electrolytic solvent in which an electrolytic salt is dissolved, in a mixing ratio of about 1:2-10 by weight.

2. A polymer electrolyte as claimed in claim 1, wherein a weight average molecular weight of said polyvinylidene fluoride-based polymer is in a range of about 50,000-1,000,000 and a polymer dispersion degree thereof is in a range of about 1-4.

3. A polymer electrolyte as claimed in claim 1, wherein said polyvinylidene fluoride-based polymer is a copolymer of polyvinylidene fluoride and hexafluoro propane, and an amount of said hexafluoro propane is in a range of about 2-30% by weight based on the total amount of said copolymer, a weight average molecular weight of said polyvinylidene fluoride-based polymer being in a range of about 50,000-1,000,000 and a polymer dispersion degree thereof being in a range of about 1-4.

4. A polymer electrolyte as claimed in claim 1, wherein said electrolytic solvent is at least one selected from the group consisting of ethylene carbonate (EC), propylene carbonate (PC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethyl methyl carbonate (EMC) and γ–butyrolactone (γ–BL).

5. A polymer electrolyte as claimed in claim 4, wherein an amount of
said ethylene carbonate is in a range of about 20-80% by weight based on the total amount of said electrolytic solvent.

6. A polymer electrolyte as claimed in claim 4, wherein an amount of at least one electrolytic solvent selected from the group consisting of said diethyl carbonate, dimethyl carbonate and ethyl methyl carbonate, is in a range of about 20-80% by weight based on the total amount of said electrolytic solvent.

7. A polymer electrolyte as claimed in claim 4, wherein an amount of said propylene carbonate or said γ-butyrolactone is in a range of about 60% by weight or less based on the amount of said ethylene carbonate.

8. A polymer electrolyte as claimed in claim 1, wherein said electrolytic salt is at least one selected from the group consisting of lithium perchlorate (LiClO₄), lithium trifluoromethane sulfonate (LiCF₃SO₃), lithium borofluoride (LiBF₄), lithium hexafluorophosphate (LiPF₆) and lithium arsenic hexafluoride (LiAsF₆).

9. A polymer electrolyte as claimed in claim 8, wherein a concentration of said electrolytic salt with respect to said electrolytic solvent is in a range of about 0.5-2M.

10. A method of manufacturing a polymer electrolyte comprising the steps of:

mixing a polyvinylidene fluoride-based polymer with an electrolytic solvent in which an electrolytic salt is dissolved, in a mixing ratio of about 1:2-10 by weight;

preparing a substantially homogeneous electrolytic slurry by stirring and
heating thus obtained mixture; and
solidifying thus obtained electrolytic slurry.

11. A method of manufacturing a polymer electrolyte as claimed in claim 10, wherein said step of mixing said polyvinylidene fluoride-based polymer with said electrolytic solvent is implemented at room temperature.

12. A method of manufacturing a polymer electrolyte as claimed in claim 10, wherein said electrolytic slurry is prepared by stirring said mixture at a temperature range of about 60-150°C for about 5 minutes – 2 hours.

13. A method of manufacturing a polymer electrolyte as claimed in claim 10, wherein a viscosity of said electrolytic slurry is in a range of about 1,000-100,000 cps.

14. A method of manufacturing a polymer electrolyte as claimed in claim 10, wherein said step of solidifying said electrolytic slurry is implemented by coating said electrolytic slurry on a substrate or a molded film and then drying.

15. A lithium polymer secondary battery comprising a cathode, an anode and a polymer electrolyte positioned between said cathode and anode and manufactured by solidifying an electrolytic slurry obtained by mixing a polyvinylidene fluoride-based polymer and an electrolytic solvent in which an electrolytic salt is dissolved, in a mixing ratio of about 1 : 2-10 by weight.

16. A lithium polymer secondary battery as claimed in claim 15, wherein said cathode is manufactured by mixing about 23-35% by weight of an active
material, about 0.5-2% by weight of a conductive material, about 15-25% by weight of said electrolytic slurry and about 40-60% by weight of a solvent.

17. A lithium polymer secondary battery as claimed in claim 15, wherein said anode is manufactured by mixing about 23-35% by weight of an active material, about 0-2% by weight of a conductive material, about 15-25% by weight of said electrolytic slurry and about 40-60% by weight of said solvent.
**INTERNATIONAL SEARCH REPORT**

**CLASSIFICATION OF SUBJECT MATTER**

**IPC**: H01M 10/22

According to International Patent Classification (IPC) or to both national classification and IPC

**FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

**IPC**: H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

WPI, EPODOC, Patdpa, Depatisnet

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<td>JP 10 284124 A2 (ASAHI GLASS CO LTD) 23 October 1998 (23.10.98) Patent abstract.</td>
<td>1,8,10,15</td>
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<td>A</td>
<td>JP 11 273453 A2 (MITSUBISHI RAYON CO LTD) 8 October 1999 (08.10.99) Patent abstract.</td>
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Further documents are listed in the continuation of Box C. ✗ See patent family annex.

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search 14 February 2002 (14.02.2002)

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