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(71) Applicant (for all designated States except US): **EBARA CORPORATION** [JP/JP]; 11-1, Haneda Asahi-cho, Ohta-ku, Tokyo 144-8510 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): **KANNO, Junichi** [JP/JP]; 1-101, 1-6-11, Zengyozaka, Fujisawa-shi, Kanagawa 251-0876 (JP). **KOMATSU, Makoto** [JP/JP]; 7-8-20-205, Shonandai, Fujisawa-shi, Kanagawa 252-0804 (JP). **HARAKAWA, Hiroaki** [JP/JP]; 1-30-33, Chitosedai, Setagaya-ku, Tokyo 157-0071 (JP). **ENDO, Naotoshi** [JP/JP]; 255-49, Dainichi, Yotsukaido-shi, Chiba 284-0001 (JP).

(74) Agent: **HOSOKAWA, Shinya**; YUASA and HARA, Section 206, New Ohtemachi Bldg., 2-1, Ohtemachi 2-chome, Chiyoda-ku, Tokyo 100-0004 (JP).

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(54) Title: CHEMICALLY MODIFIED ORGANIC POLYMERIC MATERIAL, AND METHOD AND APPARATUS FOR MANUFACTURING THE SAME

(57) Abstract: It is an object of the present invention to clarify the phenomenon that causes the functionality expected based on the amount of the desired substance introduced and so on to not be obtained when synthesizing a functional material by carrying out a radical-induced chemical reaction so as to introduce a desired substance onto an organic polymeric substrate. It is also an object of the present invention to provide a functional material, and a method and apparatus for synthesizing the same, according to which such a phenomenon is avoided. In one aspect of the present invention, there is provided an organic polymeric material comprising a chemically modified organic polymeric material substrate, wherein a response due to the chemical modification is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate..

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DESCRIPTION

CHEMICALLY MODIFIED ORGANIC POLYMERIC MATERIAL,
AND METHOD AND APPARATUS FOR MANUFACTURING THE SAME5 BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to art for a method and apparatus for introducing a chemical substance onto an already molded organic polymeric substrate by carrying out a radical-induced chemical reaction, and for a product obtained through introducing the chemical substance, in which it is verified that required functionality is introduced to the substrate by measuring the distribution of the abundance of an introduced desired substance using means enabling analysis of atoms or atomic groups constituting the desired substance in a depth direction from a surface of the product inwards.

Description of the Related Art

Various methods have been attempted for giving an already molded organic polymeric material any of various functionalities, for example a method in which functional groups are directly introduced onto the surface of the material by plasma irradiation, sulfonation or the like, a method in which the surface is chemically modified with a polymer containing the functional groups using a crosslinking polymerization method, and a method in which a monomer is graft polymerized onto a polyolefin substrate or the like.

Of these, as shown in Japanese Patent Publication No. 6-55995, a method in which an organic polymeric substrate is irradiated with ionizing radiation to produce radicals, and a chemical reaction

induced by these radicals is carried out so as to introduce any of various functionalities to the substrate is very versatile, since the method can be applied to substrates of various forms, and moreover the form of the substrate can be maintained after the reaction.

5 Furthermore, the functional groups manifesting the desired functionality are chemically bonded to the substrate, and hence there is hardly any diffusion or dissociation of these functional groups away from the substrate. The whole description in Japanese Patent Publication No. JP-B-6-55995 is incorporated herein by
10 reference.

In recent years, through the research of the present inventors, for organic polymeric materials obtained by introducing desired functionality to a substrate using a radical-induced chemical reaction as described above, some cases have been observed in which,
15 compared with the functionality expected based on the amount of the desired substance introduced onto the substrate (theoretical value), the functionality actually observed is insufficient, or is hardly manifested at all. For example, this phenomenon has been observed with functionalities such as the following: the wettability
20 (contact angle) of the surface of a thin film material onto which hydrophilic functional groups have been introduced; the ionic conduction (diffusion) rate in the film thickness direction of a thin film material onto which ion exchange groups have been introduced; the water absorption rate of a nonwoven fabric onto
25 which hydrophilic functional groups have been introduced; and the metal ion adsorption rate of a nonwoven fabric onto which cation exchange groups have been introduced.

The current state of affairs is that it has not been clarified

why the above phenomenon occurs, what state the material is in after the introduction of the functional groups, or what should be done to synthesize a functional material while avoiding the above phenomenon.

5 It is thus an object of the present invention to clarify the phenomenon that causes the functionality expected based on the amount of the desired substance introduced and so on to not be obtained when synthesizing a functional material by carrying out a radical-induced chemical reaction so as to introduce a desired
10 substance onto an organic polymeric substrate, and to provide a functional material, and a method and apparatus for synthesizing the same, according to which this phenomenon is avoided. Note that "chemical modification" in the present invention means the introduction of a desired substance onto a substrate by forming
15 chemical bonds such as covalent bonds, ionic bonds or coordinate bonds.

SUMMARY OF THE INVENTION

As a result of assiduous studies, the present inventors have
20 been the first to discover that, in a region between 1 and 100 nm in a depth direction of a surface layer of a material for which the expected functionality (theoretical value) is not obtained, there is a region in which the amount of a desired substance introduced in is very low or the desired substance has not been introduced
25 at all. The present inventors have further discovered that in the case that there is such a region that has not been chemically modified in the depth direction, it is very difficult to verify the presence of this region using a scanning electron microscope (SEM-XMA) or

infrared spectroscopy (IR) since these techniques cannot analyze only the region of 1 nm to 100 nm, but rather the presence of this region can only be verified by analyzing the surface using X-ray photoelectron spectroscopy (XPS), a transmission electron
5 microscope (TEM) or the like. As a result of further assiduous studies, the present inventors have also discovered that such a region is brought about due to oxygen molecules present in a very small amount in the system during reaction. Furthermore, the present inventors have discovered that the above problem can be solved by
10 controlling the oxygen concentration to be lower than conventionally during a process from irradiation with ionizing radiation up to completion of the reaction, thus accomplishing the present invention.

In the case of carrying out, for example, a radical-induced
15 graft polymerization reaction on an organic polymeric substrate, generally, if the oxygen concentration is below 1000 ppm, then even if some of the radicals on the substrate are consumed by oxygen molecules, radicals remaining in a crystalline portion of the substrate undergo migration through the substrate, and then the
20 polymerization reaction proceeds with these radicals as starting points, and hence hitherto it has been thought that there is basically no problem. For example, in the case of introducing sulfonic acid groups onto polyethylene fibers by graft polymerizing glycidyl methacrylate onto the polyethylene fibers using an impregnation
25 vapor phase method and then carrying out sulfonation treatment, hardly any difference has been found in results of analysis of the elemental distribution by SEM-XMA or the amount of sulfonic acid groups introduced between the case that the oxygen concentration

in the vapor phase is 1000 ppm and the case that this oxygen concentration is 100 ppm.

The present inventors have carried out detailed analysis of materials for which the expected functionality (theoretical value) is not obtained, and from the results of analysis of the elemental distribution on the material surface by XPS or TEM, have been the first to discover that in a very narrow region of from 1 nm to 100 nm in the depth direction, there is a region in which little or none of an element originating from the desired substance is present. In the case that this region has a depth of not more than 1 μ m in particular, it is very difficult to find the region through analysis of the elemental distribution using SEM-XMA.

Furthermore, the present inventors thought that such a region is present because the desired reaction does not proceed in only this region, and thought that the cause of this was a very small amount of oxygen molecules that hitherto had not been considered to be a problem. It is thought that the occurrence of such a phenomenon even if the oxygen concentration is less than 1000 ppm as conventionally has as its background the reaction rate between oxygen molecules and radicals on the polymeric substrate being very fast.

The present inventors thus carried out introduction of a desired substance while controlling the oxygen concentration in at least one of a radical generation step and a radical-induced reaction step to be lower than conventionally, and analyzed the polymeric material obtained using XPS (or TEM), whereupon it was discovered that a region as described above ceases to be present upon controlling the oxygen concentration in this way. Furthermore, for polymeric materials thus obtained, the present inventors

evaluated functionalities such as the wettability (contact angle) of the surface of a thin film material onto which hydrophilic functional groups have been introduced, the ionic conduction (diffusion) rate in the film thickness direction of a thin film material onto which ion exchange groups have been introduced, the water absorption rate of a nonwoven fabric onto which hydrophilic functional groups have been introduced, and the metal ion adsorption rate of a nonwoven fabric onto which cation exchange groups have been introduced, whereupon it was found that better results than in the case of a conventional method were exhibited.

Through a desired functionality being introduced well as described above, an organic polymeric material according to the present invention can be suitably used in various applications. For example, in the case that the desired substance introduced comprises cation exchange groups, by introducing the cation exchange groups in a region of the substrate of depth not more than 20 nm, the organic polymeric material according to the present invention can be suitably used as a polyelectrolyte film for a polymer electrolyte fuel cell (PEFC). By introducing the cation exchange groups in a region of depth not more than 50 nm, the organic polymeric material according to the present invention can be suitably used as a polyelectrolyte film for electrodialysis or a separator for a secondary cell. In the case that the desired substance introduced comprises ion exchange groups or chelate groups, by introducing these functional groups in a region of depth not more than 50 nm, the organic polymeric material according to the present invention can be suitably used as a material for removing metal ions.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a drawing showing an example of the constitution of a continuous conveyance type grafting reaction apparatus;

FIG. 2 is a flowchart of an operation control method using measured oxygen concentration values for applying a method of the present invention to a continuous conveyance type reaction process;

FIG. 3 is a conceptual drawing of the operation control method using measured oxygen concentration values for applying the method of the present invention to the continuous conveyance type reaction process;

FIG. 4 is a drawing showing the form of a glove box used in the Examples;

FIG. 5 is a drawing showing the constitution of an ion conductivity measuring apparatus used in the Examples;

FIG. 6 is a graph showing ion conductivity test results for Example 5; and

FIG. 7 is a drawing schematically illustrating a water absorption rate measurement method used in the Examples.

DETAILED DESCRIPTION OF THE INVENTION

Following is a detailed description of various forms of the present invention.

For the case of a method of introducing a chemical substance onto an organic polymeric substrate by carrying out a radical-induced chemical reaction, and a product obtained through this introduction, the present invention relates to a product for which it has been verified that required functionality has been introduced to the substrate by measuring the distribution of the abundance of an

introduced desired substance using means enabling analysis of atoms or atomic groups constituting the desired substance in a depth direction from a surface of the product inwards, and a method and apparatus for manufacturing the product.

5 The present invention relates to a method of introducing a desired substance giving any of various added functionalities to an organic polymeric substrate by generating radicals through radical-generating means on the organic polymeric substrate, or simultaneously on both the organic polymeric substrate and the
10 desired substance to be introduced, or on the desired substance to be introduced, and carrying out reaction taking the radicals as starting points, so as to form chemical bonds such as covalent bonds, ionic bonds or coordinate bonds, wherein the oxygen concentration is controlled in the radical generation step and/or
15 the radical-induced chemical reaction step. By holding the oxygen concentration in these steps in the range of from 1 to 200 ppm in the radical generation step and from 1 to 100 ppm in the radical-induced chemical reaction step, the desired substance can be introduced also in a region of from 1 to 100 nm in a depth direction
20 from a surface of the substrate inwards.

 Furthermore, another form of the present invention relates to, for atomic groups constituting a desired substance having functionality introduced onto a product manufactured using the above method, measuring the amount of an element constituting the
25 introduced atomic groups in a depth direction from a surface of the product inwards using X-ray photoelectron spectroscopy (XPS) so as to verify the presence of the atomic groups, and thus measuring that a sufficient amount of the atomic groups for the desired

application are present on the organic polymeric substrate compared with before the reaction.

In the present invention, as the radical-generating means, any exciting means such as heating, ultraviolet radiation, ionizing radiation, a laser, or an ion beam may be used. However, using heating or ultraviolet radiation is not very desirable, since the excitation source generally has an energy level of not more than 10^{-2} eV in the case of heating or in a range of 3 to 10 eV in the case of a commercially available ultraviolet radiation irradiating device, but such an energy level is too low to introduce chemical substances in the depth direction from a surface of the product inwards in the present invention, and moreover a chemical that assists radical generation such as an initiator may be required. A laser or an ion beam does have a sufficient energy level, but is not very desirable for reasons such as the apparatus being complex and expensive, the irradiation area and depth being narrow and shallow and hence there being structural restrictions, and the constituent material being prone to becoming radioactive. Use of ionizing radiation is suitable, since the energy level that can be applied is at 10^3 to 10^6 eV, which is sufficiently high compared with the bond energy of covalent bonds in the organic polymeric substrate or the desired substance, such ionizing radiation is currently widely used in industry, and an initiator does not have to be used.

A method for manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate according to one embodiment of the present invention comprises putting the substrate into container that can be isolated from the outside environment and in which the oxygen concentration can be

held lower than that outside, generating radicals on the substrate in part of the container, and then moving the substrate into another part of the container, and chemically modifying the substrate through a radical-induced reaction, and wherein the oxygen concentration
5 of the atmosphere in which the chemical modification is carried out is in a range of from 1 to 100 ppm.

A method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate according to another embodiment of the present invention comprises
10 putting the substrate into container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, generating radicals on the substrate in part of the container, and then moving the substrate into another part of the container, and chemically modifying the substrate through
15 a radical-induced reaction, and wherein the oxygen concentration of the atmosphere in which the radicals are generated is in a range of from 1 to 200 ppm.

A method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate
20 according to another embodiment of the present invention comprises putting the substrate into a container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, generating radicals on the substrate in part of the container, and then moving the substrate into another
25 part of the container, and chemically modifying the substrate through a radical-induced reaction, and wherein the oxygen concentration of the atmosphere in which the chemical modification is carried out is in a range of from 1 to 100 ppm, and the oxygen concentration

of the atmosphere in which the radicals are generated is in a range of from 1 to 200 ppm.

As the container, a single container which is partitioned into a portion in which the radicals are generated on the substrate and a portion in which the chemical modification is carried out. Or, the container may comprise a container in which the radicals are generated on the substrate and a separate container in which the chemical modification is carried out, and an apparatus containing a connecting section that is isolated from the outside environment and through which the substrate can be moved while holding the oxygen concentration of the atmosphere therein in a range of from 1 to 100 ppm, may be used.

Thus, in the above mentioned method of manufacturing an organic polymeric material, the container also may comprise a container in which the radicals are generated on the substrate and a separate container in which the chemical modification is carried out, and the method may further comprise moving the substrate from the container in which the radicals are generated to the container in which the chemical modification is carried out via a connecting section that is isolated from the outside environment and through which the substrate can be moved while holding the oxygen concentration of the atmosphere therein in a range of from 1 to 100 ppm.

Further, in the method of the present invention, radical generation and chemical modification may be conducted simultaneously. Thus, a method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate according to another embodiment of the present

invention comprises putting the substrate into a container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, and generating radicals on the substrate while bringing the substrate and a reactant
5 for the chemical modification into contact with one another in part of the container, and wherein the oxygen concentration of the atmosphere in which the chemical modification is carried out is in a range of from 1 to 100 ppm.

Radical-induced chemical reaction includes, for example,
10 graft polymerization.

Oxygen concentration of the atmosphere in which the chemical modification is carried out is preferably in a range of from 1 to 80 ppm, more preferably from 1 to 50 ppm, further preferably from 1 to 30 ppm. Oxygen concentration of the atmosphere in which the
15 radicals are generated is preferably in the range of from 1 to 100 ppm, more preferably from 1 to 80 ppm, further preferably from 1 to 50 ppm.

The substrate may be a sheet-shaped material of a fiber aggregate such as woven or non-woven fabric or a film, and at least
20 one of a step of supplying the substrate into a space in which the reaction is carried out, a step of generating the radicals on the substrate, a step of carrying out the chemical modification on the substrate, and a step of conveying a product out may be carried out continuously.

25 As a method for holding oxygen concentration of a space in which the chemical modification is carried out or a space in which the radicals are generated in the above range, a method of supplying inert gas of oxygen concentration of the above range or of lower

oxygen concentration within the range of from 1 ppb to 100 ppm into the space to thereby replace gas inside the space, may be used. Or as another method, a method of supplying inert gas of oxygen concentration of the above range or of lower oxygen concentration within the range of from 0.1 ppm to 100 ppm into the space, thereby exhausting gas in the space, subjecting the exhausted gas to deoxygenation treatment, and then returning the gas into the space, thus carrying out circulation and replacement of the gas in the space, may be used. Deoxygenation treatment of the gas includes passing the gas through a oxygen adsorption tower or irradiating electron beam to the gas. The replacement of the gas or circulation replacement of the gas is preferably conducted continuously during operation of radical generation and chemical reaction. The inert gas may be nitrogen gas of purity not less than 99.99%.

Ionizing radiation that can be used in the present invention includes a neutron beam, α -rays, β -rays, γ -rays, X-rays, and an electron beam. However, with a neutron beam, α -rays, β -rays or γ -rays, a radioisotope must be used, and hence there are constraints on the structure of the irradiating device, and moreover there are strong legal constraints on use. X-rays and an electron beam are preferable, since these are widely used in industry, the degree of freedom over the shape of the irradiating chamber is high and hence process design is easy, and thus control of the oxygen concentration in the radical generation step is also easy. An electron beam is most preferable, since the efficiency of energy conference is high due to the beam quality being good. The radiation dose is preferably in a range of from 10 to 500 kGy, more preferably from 50 to 200 kGy.

As methods of radical generation using radiation in the present invention, there are a pre-irradiation method in which radicals are generated in the organic polymeric substrate in advance, the organic polymeric substrate is stored such that the radicals that have been generated therein are preserved, and then the organic polymeric substrate in which the radicals have been generated and the desired substance are brought into contact with one another to bring about reaction, and a simultaneous irradiation method in which radicals are generated under the presence of both the organic polymeric substrate and the desired substance. Either method can be used in the present invention, or the simultaneous irradiation method and the pre-irradiation method may be combined in a continuous process. Regarding the storage temperature of the organic polymeric substrate after the radical generation in the pre-irradiation method, to suppress decay of the radicals, a temperature above 40°C is undesirable, and hence the storage temperature is preferably in a range of -196 to 40°C, more preferably -80 to 30°C. Regarding the storage time, the lower the storage temperature, the longer storage is possible; the storage time is preferably from 2 minutes to 6 months, and at a temperature around room temperature of 15 to 30°C is preferably in a range of 1 to 30 minutes. The oxygen concentration during the storage is preferably lower than the oxygen concentration in atmospheric air, with from 0.1 to 5% being suitable, and from 1 to 200 ppm being preferable, with from 1 to 100 ppm being more preferable, from 1 to 80 ppm being further preferable, and from 1 to 50 ppm being further more preferable.

Examples of methods of bringing the organic polymeric substrate and the chemical substance into contact with one another

when carrying out the radical-induced chemical reaction in the present invention include a liquid phase method in which the reaction is carried out with the organic polymeric substrate immersed in a solution of the chemical substance; a vapor phase method in which
5 the reaction is carried out by bringing the organic polymeric substrate into contact with a vapor of the chemical substance, an impregnation vapor phase method in which the organic polymeric substrate is immersed in a solution of the chemical substance, and then the organic polymeric substrate is taken out from the solution
10 and reaction is carried out in the vapor phase using solution of the chemical substance remaining in the organic polymeric substrate, and a coating method in which a solution containing the chemical substance or a solid containing the chemical substance is coated onto a surface of the organic polymeric substrate so as to bring
15 about reaction; any of these methods can be suitably used.

In the present invention, as the method of controlling the oxygen concentration in the radical generation step, for example one of the following methods can be adopted: a method in which the organic polymeric substrate piece is put into a container
20 (hereinafter referred to as an "irradiating container") made of a material having an oxygen permeability coefficient of not more than 10^{-5} mol·cm/m²·sec·Pa, and then the gas inside the container is replaced with an inert gas such as nitrogen or argon; a method in which an irradiating chamber of an irradiating device is made to
25 have a structure surrounded by a wall able to isolate the irradiating chamber from atmospheric air, and the irradiating chamber has an inert gas introduced therein and is exhausted so as to replace air in the irradiating chamber with the inert gas; and a method in which

the interior of an irradiating container is exhausted so as to reduce the pressure in the irradiating container and thus reduce the oxygen partial pressure in the irradiating container. As the method of measuring the oxygen concentration, for example one of the following methods can be adopted: a method in which when replacing the gas inside an irradiating container, the replacement is carried out in a glove box into which the inert gas has been introduced, and the oxygen concentration in the glove box is measured using oxygen concentration measuring means; a method in which the pressure in the irradiating container is measured and the oxygen concentration is calculated from the oxygen partial pressure; and a method in which the oxygen concentration in an irradiating chamber is monitored using oxygen concentration measuring means connected by a sampling pipe made of a material having an oxygen permeability coefficient of not more than 10^{-5} mol·cm/m²·sec·Pa (e.g. stainless steel, Teflon (registered trademark), nylon, etc.). Such monitoring may be carried out continuously while carrying out the irradiation. The oxygen concentration in the radical generation step is in a range of from 1 to 200 ppm in the present invention, with from 1 to 100 ppm being preferable, from 1 to 80 ppm being more preferable, and from 1 to 50 ppm being further more preferable.

In order to maintain the above mentioned oxygen concentration in radical generation step, for example, oxygen concentration in a container is continuously monitored during operation of irradiation by means of the above mentioned oxygen concentration measuring means, and when the oxygen concentration approaches the freely chosen set value (upper limit of the predetermined oxygen concentration range), flow rate of the inert gas introduced into

the container may be increased by opening/closing a solenoid valve or the like in accordance with the way in which the oxygen concentration approaches the set value, whereby the oxygen concentration can be maintained within the predetermined range.

5 As the method of controlling the oxygen concentration in the radical-induced chemical reaction step, the same method as for the radical generation step may be used. Further, for example, a method in which the irradiated organic polymeric substrate and a solution of the chemical substance are introduced into and sealed in a reaction
10 vessel in a glove box as above while measuring the oxygen concentration may also be used. The oxygen concentration in the chemical reaction step is preferably in a range of from 1 to 100 ppm, with from 1 to 80 ppm being preferable, from 1 to 50 ppm being more preferable, and from 1 to 30 ppm being further more preferable.

15 As a method maintain the above mentioned oxygen concentration in chemical reaction step, for example, the same method as in the radical generation step mentioned above may be used.

In the case of constructing an industrial mass production process, for example a continuous conveyance type reaction process
20 as proposed by the present inventors (U.S. Patent No. 6,659,751) can be used. The descriptions in U.S. Patent No. 6,659,751 are incorporated herein by reference. An example of the constitution of such a continuous conveyance type reaction process is shown in FIG. 1. The continuous conveyance type reaction process is for
25 carrying out radical generation using a pre-irradiation method, and then bringing about reaction by bringing a roll-shaped organic polymeric substrate and a chemical substance into contact with one another using an impregnation vapor phase method, and is constituted

from four steps as pivotal elements, which can also be used in another system. First is a rolling out step in which the roll-shaped organic polymeric substrate is rolled out and thus continuously supplied in; second is an ionizing radiation irradiation step in which radicals
5 are generated in the rolled out organic polymeric substrate; third is a chemical reaction step in which the irradiated organic polymeric substrate and the chemical substance are brought into contact with one another to bring about a radical-induced chemical reaction; and fourth is a rolling up step in which the product obtained through
10 the reaction is rolled back up into the form of a roll to finish. As shown in Fig. 1, chemical reaction step may be divided into an impregnation step where substrate is impregnated with chemical substance and a reaction step where radical-induced chemical reaction is proceeded. The pathway from an irradiating device that
15 carries out the irradiation with the ionizing radiation to generate the radicals to the reactor in which the radical-induced chemical reaction is carried out, and the devices are made to have a container-like structure surrounded by a wall that isolates the inside thereof from atmospheric air, and replacement of the gas
20 therein is carried out by introducing an inert gas therein and exhausting, so that the oxygen concentration along the conveyance pathway and inside the devices can be controlled. Here, to increase the efficiency of the replacement of the gas inside, an internal circulating device such as a fan may be installed in the devices.
25 Replacement of gas inside is preferably conducted continuously. In each device where each of the above mentioned step is conducted (in Fig. 1, irradiation device, impregnation device and reaction device), oxygen concentration can be maintained within the

predetermined range by attaching oxygen concentration meter to the each device, and continuously monitoring oxygen concentration in the device, and when the oxygen concentration approaches the freely chosen set value (upper limit of the predetermined oxygen
5 concentration range), increasing flow rate of the inert gas introduced into the container by opening/closing a solenoid valve or the like in accordance with the way in which the oxygen concentration approaches the set value.

As with the devices themselves, connecting sections between
10 the devices that carry out the respective steps may also have a structure surrounded by a wall that isolates the inside thereof from atmospheric air, or a sealing structure or the like may be provided at the connecting sections to thereby keep each device separate airtight condition, whereby an effect of it being possible
15 to reduce the amount of the inert gas used can be expected, and additionally an effect of it being possible to maintain predetermined oxygen concentration for each device can also be expected. A specific example of such a sealing structure is that in Japanese Patent Application No. 2004-203507, which is a prior patent case
20 from the present inventors. The descriptions in Japanese Patent Application No. 2004-203507 are incorporated herein by reference. As the method of measuring the oxygen concentration inside the devices in the present invention, as with the irradiating chamber, a method in which the oxygen concentration is monitored using oxygen
25 concentration measuring means connected using a sampling pipe made of a material having an oxygen permeability coefficient of not more than 10^{-5} mol·cm/m²·sec·Pa (e.g. stainless steel, Teflon (registered trademark), nylon, etc.) can be adopted. As in the irradiation step,

the monitoring of the oxygen concentration may be carried out continuously.

The present invention also relates to an apparatus for conducting a method of the present invention as explained above to thereby produce a chemically modified organic polymeric material.

Thus, another embodiment of the present invention relates to an organic polymeric material chemical modification apparatus for manufacturing a film-shaped organic polymeric material by chemically modifying an organic polymeric material substrate, the apparatus comprising:

an ionizing radiation irradiating section that is disposed in a first container that isolates the substrate from the outside environment and in which the oxygen concentration can be held lower than that outside, and is for generating radicals on the organic polymeric material substrate;

a chemical modification section that is disposed in a second container that isolates the substrate from the outside environment and in which the oxygen concentration can be held lower than that outside, and is for carrying out chemical modification through a reaction induced by the radicals; and

a connecting section that is disposed in a third container that isolates the substrate from the outside environment and in which the oxygen concentration can be held lower than that outside, and connects the container in which the ionizing radiation irradiating section is disposed to the container in which the chemical modification section is disposed, enabling the substrate to be moved therebetween, wherein

one of the first container in which the ionizing radiation

irradiating section is disposed, the second container in which the chemical modification section is disposed, and the third container in which the connecting section is disposed is provided with at least one inert gas supply port for supplying an inert gas into
5 the container, and at least one exhaust port for exhausting gas from the container, and wherein

the apparatus also comprising a mechanism to hold the oxygen concentration of the gas in the first container in which the ionizing radiation irradiating section is disposed in a range of from 1 ppm
10 to 200 ppm, and/or the oxygen concentration of the gas in the second container in which the chemical modification section is disposed in a range of from 1 ppm to 100 ppm.

The chemical modification section may be divided into impregnation section and reaction section, and each section may
15 be disposed in separate container and the containers may be connected by a connecting section. In this case, both of the container in which impregnation section is disposed and the container in which reaction section is disposed have a mechanism to hold the oxygen concentration of the gas in the container in a range of from 1 ppm
20 to 100 ppm.

An ionizing radiation irradiating section, an chemical modification section and a conveyance section may be disposed in one container. Thus, another embodiment of the present invention relates to an organic polymeric material chemical modification
25 apparatus for manufacturing a film-shaped organic polymeric material by chemically modifying an organic polymeric material substrate, the apparatus comprising:

a container that isolates the substrate from the outside

environment and in which the oxygen concentration can be held lower than that outside;

an ionizing radiation irradiating section that is disposed in the container, and is for generating radicals on the organic
5 polymeric material substrate;

a chemical modification section that is disposed in the container, and is for chemically modifying the substrate through a reaction induced by the radicals; and

a conveyance section that is disposed in the container, and
10 is for conveying the substrate from the ionizing radiation irradiating section into the chemical modification section, wherein

the container is provided with an inert gas supply port for supplying an inert gas into the container, and an exhaust port for exhausting gas from the container, and wherein

15 the oxygen concentration of the gas in the container is held in a range of from 0.1 ppm to 100 ppm.

In the apparatuses as explained above, as the mechanism to hold oxygen concentration of gas inside the container in the predetermined range, for example, a system in which oxygen
20 concentration meter is attached to the container, and oxygen concentration in the container is continuously monitored, and when the oxygen concentration approaches the freely chosen set value (upper limit of the predetermined oxygen concentration range), increasing flow rate of the inert gas introduced into the container
25 by opening/closing a solenoid valve or the like in accordance with the way in which the oxygen concentration approaches the set value.

The organic polymeric material chemical modification apparatuses as mentioned above may further comprises an oxygen

concentration meter that continuously monitors the oxygen concentration of the gas in the ionizing radiation irradiating section and/or the chemical modification section, and further comprises a warning device for issuing a warning if the oxygen concentration deviates from a prescribed concentration range. The apparatus may further comprises an oxygen concentration meter that continuously monitors the oxygen concentration of the gas in the ionizing radiation irradiating section and/or the chemical modification section, and further comprises a shutdown device for stopping the irradiation with the ionizing radiation and/or stopping the chemical modification reaction if the oxygen concentration deviates from a prescribed concentration range. Further, the apparatuses may further comprises an oxygen concentration meter that monitors the oxygen concentration of the gas in the ionizing radiation irradiating section and/or the chemical modification section, and further comprises a control device for controlling commencement of operation of the apparatus to be operational when the oxygen concentration of the gas in each of the ionizing radiation irradiating section and the chemical modification section is within a prescribed concentration range.

The present invention also relates a program for operating the apparatus as explained above. Thus, another embodiment of the present invention relates a computer-readable apparatus operation program for the organic polymeric material chemical modification apparatus as explained above, for implementing a step of making the oxygen concentration of the gas in each of the ionizing radiation irradiating section, the chemical modification section and the connecting section be within a prescribed concentration range by

replacing the gas in each of the ionizing radiation irradiating section, the chemical modification section and the connecting section with an inert gas in which the oxygen concentration is within a prescribed concentration range, a step of moving a substrate that has been conveyed in from a substrate supply section into the ionizing radiation irradiating section, and irradiating the substrate with a prescribed amount of ionizing radiation by adjusting an irradiation source and the irradiation time, thus generating radicals on the substrate, a step of moving the substrate on which the radicals have been generated into the chemical modification section, bringing the substrate into contact with a prescribed reactant containing a chemical species required in chemical modification induced by the radicals, and carrying out the chemical modification at a prescribed reaction temperature for a prescribed reaction time, thus producing a chemically modified product, and a step of conveying the chemically modified product out using a product conveying section. The program may further comprise a program unit for implementing the step of issuing a warning if the oxygen concentration deviates from a prescribed concentration range. The program may further comprise a program unit for implementing the step of stopping the irradiation with the ionizing radiation and/or stopping the chemical modification reaction if the oxygen concentration deviates from a prescribed concentration range. The program may further comprise a program unit for implementing the step of controlling commencement of operation of the apparatus to be operational when the oxygen concentration of the gas in each of the ionizing radiation irradiating section and the chemical modification section is within a prescribed concentration range.

The reaction time used in the radical-induced chemical reaction step varies depending on the combination of the organic polymeric substrate and the chemical substance, but from 5 minutes to 24 hours is suitable, preferably 10 minutes to 6 hours, more preferably 15 minutes to 2 hours. The reaction temperature used in this step may be any temperature from -20° C up to the decomposition temperature of the chemical substance, but from 20 to 120° C is suitable, preferably 30 to 80° C, more preferably 40 to 70° C.

Oxygen concentration measuring means used in the present invention may be any commercially available oxygen concentration meter, but it must be possible to measure oxygen concentrations below 100 ppm. Types include a magnetic type (POM6E made by Japan Air Gases Ltd., ZKG made by Fuji Electric Instruments Co., Ltd., etc.), a zirconia type (LC-750 made by Toray Engineering Co., Ltd., IS-700 made by Iijima Electronics Corporation, etc.), and a galvanic type (MC-7G made by Iijima Electronics Corporation, MKI-50 made by Japan Air Gases Ltd, etc.). However, from the viewpoint of the oxygen concentration measurement range required in the present invention, the magnetic type lacks sensitivity. Moreover, the sample gas from the chemical reaction step may contain flammable gas, in which case the oxygen concentration cannot be measured accurately using the zirconia type. In the present invention, the galvanic type, which has a sufficient oxygen concentration measurement range, and for which there are no problems with the measurement even if the sample gas contains flammable gas, is thus suitable. In the case of carrying out monitoring for the chemical reactor, to prevent contamination due to evaporation or scattering of the chemical substance, a cold trap, a mist separator or the

like can be installed in the gas sampling pipe so as to extend the lifetime of the oxygen concentration meter.

Regarding the reaction solution used in the present invention, the dissolved oxygen concentration in the solvent must be reduced
5 by aerating the solvent with an inert gas before use, and it is preferable to measure the dissolved oxygen concentration using oxygen concentration measuring means. The dissolved oxygen concentration in the reaction solvent used in the present invention is preferably in a range of from 0.1 to 8 ppm, with from 0.1 to
10 4 ppm being suitable, and from 0.1 to 1 ppm being more preferable. To prevent oxygen in piping from getting into the device in which the reaction is carried out when transferring the reaction solution into the device from a container having a function of storing the reaction solution and isolating the reaction solution from
15 atmospheric air, the reaction solution that has been aerated with the inert gas can be fed into the piping so as to force out gas residing in the piping, thus preventing from getting into the device from the piping. More preferably, a method can be adopted in which the gas in the piping is replaced with an inert gas, and then the
20 reaction solution is fed in.

As a material for the organic polymeric substrate that can be used in the present invention, any organic polymeric material from which radicals can be generated can be used; for example, polyolefin resins, halogenated polyolefin resins, and so on, which
25 are easily shaped and are widely distributed, are suitable, with it being easy to use polyethylene and polypropylene, which are widely used plastics, and fluororesins (Teflon (registered trademark) made by Mitsui DuPont Fluorochemicals, the Neoflon series made by Daikin,

etc.), which are engineering plastics. A polyvinyl alcohol resin (Bovlon made by Nippon Synthetic Chemical Industry Co., Ltd., etc.), a polyvinyl alcohol-ethylene copolymer resin (Eval made by Kuraray Co., Ltd., etc.), a polyvinyl chloride resin, a polyester resin, a nylon resin, or the like can also be used. An organic polymeric substrate of any form may be used, for example granules, a rod-like form, a woven fabric or nonwoven fabric, a film or sheet, fibers or yarn, hollow fibers, a straw-like form, or a foam. In the case of adopting the continuous conveyance type process described earlier, a form that can be put into a roll is most suitable.

As chemical substances that can be used in the present invention and made to undergo the radical-induced chemical reaction with the organic polymeric substrate, for example any polymerizable monomer having a carbon-carbon double bond therein can be used. Examples include polymerizable monomers having functional atomic groups such as ion exchange groups or hydrophilic groups, for example (meth)acrylic acid, sodium styrenesulfonate, sodium vinylsulfonate, vinylbenzyltrimethylammonium chloride, diethylaminoethyl methacrylate, acrylamide, hydroxyethyl methacrylate, N-vinylacetamide, and N-vinylpyrrolidone. In the case of using such a chemical substance, the desired substance can be introduced onto the organic polymeric substrate through only the chemical reaction step. Alternatively, it is also possible to use a polymerizable monomer that does not itself have the desired functional atomic groups but instead has atomic groups that constitute a precursor able to be converted into the desired substance through an additional subsequent step, carry out the radical-induced chemical reaction according to the present invention, and then use a prescribed chemical

to form the product having the desired substance thereon. Examples of polymerizable monomers for which this method can be used include glycidyl methacrylate, styrene, chloromethylstyrene, and vinyl acetate. For example, it is possible to introduce glycidyl

5 methacrylate onto the organic polymeric substrate as polymer side chains through a radical-induced chemical reaction, and then, for example, react with dimethylamine or iminodiethanol so as to form a product having weakly basic amino groups on the polymer side chains.

Similarly, it is possible to introduce styrene onto the organic

10 polymeric substrate as polymer side chains, and then carry out a sulfonation reaction with a chlorosulfonic acid solution or the like so as to introduce cation exchange groups. Furthermore, it is possible to introduce chloromethylstyrene onto the organic

polymeric substrate as polymer side chains, and then form a quaternary

15 salt with trimethylamine or the like so as to introduce anion exchange groups. If a chelating agent such as iminodiacetic acid is used after carrying out the radical-induced chemical reaction, then chelate groups such as iminodiacetic acid groups can be introduced.

It is also possible to bring a polymer obtained by polymerizing

20 a polymerizable monomer as above into contact with the organic polymeric substrate in the form of a solution or in a solid state using a coating method, and generate radicals using a simultaneous irradiation method so as to introduce the chemical substance or desired substance onto the surface of the substrate.

25 An example of an operation control method using measured oxygen concentration values for applying the method according to the present invention to a continuous conveyance type reaction process includes a method for which a flowchart is shown in FIG. 2 and a conceptual

drawing of an example of the application is shown in FIG. 3. In the example shown in FIGS. 2 and 3, a freely chosen threshold value for an oxygen concentration range that is to be maintained is inputted into an oxygen concentration meter as a set value, a signal is
5 outputted if the oxygen concentration exceeds the set value, the signal is received by a control console of the irradiating device or the reactor, and a warning is issued, or operation of the apparatus is stopped. Alternatively, a method in which only the measured oxygen concentration value is sent from the oxygen concentration
10 meter to the control console, this measured oxygen concentration value is compared with a freely chosen set value that has been inputted into the control console in advance, and a warning is issued or operation is stopped if the measured oxygen concentration value exceeds the set value may also be adopted; either of these systems
15 can be selected. In the case of stopping operation, it is preferable to stop the irradiation, and then stop operation of the reactor once it has been verified that the irradiation has been stopped. This is to prevent deformation or breakage of the organic polymeric substrate through excessive irradiation with the ionizing radiation.
20 Furthermore, setup may be carried out such that operation of the apparatus can only be commenced when the oxygen concentration is below the freely chosen set value, in which case operational misses can be prevented. The oxygen concentration in each of the devices can also be held constant using the measured oxygen concentration
25 value. The flow rate of the inert gas introduced into each of the devices may be changed to a preset flow rate by opening/closing a solenoid valve or the like when the oxygen concentration approaches the freely chosen set value, this being in accordance with the way

in which the oxygen concentration approaches the set value, whereby the oxygen concentration range can be kept from exceeding the set value.

The chemically-modified organic polymeric material
5 obtainable by a method of the present invention includes the following.

1. An organic polymeric material comprising a chemically modified organic polymeric material substrate, wherein a response due to the chemical modification is detected by X-ray photoelectron
10 spectroscopy (XPS) for a surface layer of the substrate.

2. An organic polymeric material according to the above item 1, wherein a region of from 1 to 100 nm in a depth direction of a surface layer of the substrate is chemically modified.

3. The organic polymeric material according to the above
15 item 1 or 2, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

4. The organic polymeric material according to any of the above items 1 to 3, wherein the organic polymeric material is a film-shaped organic polymeric material comprising a chemically
20 modified film-shaped organic polymeric material substrate.

5. The film-shaped organic polymeric material comprising a chemically modified film-shaped organic polymeric material substrate according to the above item 4, wherein a region of from 0.02 to 0.5% of the film thickness in a depth direction of a surface
25 layer of the substrate is chemically modified.

6. The organic polymeric material according to the above item 4 or 5, wherein the surface layer comprises layers on both surfaces.

7. The organic polymeric material according to any of the above items 4 through 6, wherein the film-shaped substrate comprises a polyolefin and/or a halogenated polyolefin.

8. An organic polymeric material comprising a fiber or
5 an assembly of fibers obtained by chemically modifying an organic polymeric material substrate having the form of a fiber or an assembly of fibers, wherein a response due to the chemical modification is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

10 9. The organic polymeric material according to the above item 8, wherein a region of from 1 to 100 nm in a depth direction of a surface layer of the fibrous substrate is chemically modified.

10. The organic polymeric material comprising a fiber or
15 an assembly of fibers obtained by chemically modifying an organic polymeric material substrate having the form of a fiber or an assembly of fibers according to the above item 8 or 9, wherein from 0.02 to 0.5% of the fiber diameter in a depth direction of a surface layer of the fibrous substrate is chemically modified.

11. The organic polymeric material according to any of the
20 above items 8 to 10, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

12. The organic polymeric material according to any of the
above items 1 through 11, wherein in the chemically modified organic polymeric material, the chemical modification includes a
25 radical-induced chemical reaction.

13. The organic polymeric material according to the above item 12, wherein means for generating the radicals is irradiation with ionizing radiation.

14. The organic polymeric material according to any of the above items 12 or 13, wherein the radical-induced chemical reaction is graft polymerization.

15. The organic polymeric material according to the above
5 item 14, wherein grafted side chains introduced onto the substrate through the graft polymerization are further chemically modified.

16. The organic polymeric material according to any of the above items 1 through 15, wherein in the chemically modified organic polymeric material, the chemical modification comprises
10 introduction of ion exchange groups.

17. The organic polymeric material according to any of the above items 1 through 15, wherein in the chemically modified organic polymeric material, the chemical modification comprises introduction of ligands.

15 18. A polyelectrolyte film comprising the organic polymeric material according to any of the above items 1 through 16 obtained by introducing ion exchange groups onto the organic polymeric material substrate, wherein the ion exchange groups are introduced through reaction including a radical-induced chemical reaction.

20 19. A polyelectrolyte film comprising an organic polymeric material substrate having ion exchange groups introduced thereon, wherein a response due to the introduction of the ion exchange groups is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

25 20. The polyelectrolyte film according to the above item 19, wherein the ion exchange groups are introduced in a region between 1 and 10 nm in a depth direction of a surface layer of the substrate.

21. A polyelectrolyte film comprising an organic polymeric

material substrate having ion exchange groups introduced thereon according to the above item 19 or 20, wherein the ion exchange groups are introduced in a region of from 0.003 to 0.05% of the film thickness in a depth direction of a surface layer of the substrate.

5 22. The polyelectrolyte film according to any of the above items 19 through 21, wherein the surface layer comprises layers on both surfaces.

 23. The polyelectrolyte film according to any of the above items 19 through 22, wherein the substrate comprises a polyolefin
10 and/or a halogenated polyolefin.

 24. A battery separator for secondary cell comprising the organic polymeric material according to any of the above items 1 through 16 obtained by introducing ion exchange groups onto the organic polymeric material substrate, wherein the ion exchange
15 groups are introduced through reaction including a radical-induced chemical reaction.

 25. A battery separator for secondary cell comprising an organic polymeric material substrate having ion exchange groups introduced thereon, wherein a response due to the introduction of
20 the ion exchange groups is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

 26. The battery separator for secondary cell according to the above item 25, wherein the ion exchange groups are introduced in a region of from 1 to 50 nm in a depth direction of a surface
25 layer of the substrate.

 27. A battery separator for secondary cell according to the above item 25, wherein the ion exchange groups are introduced in a region of from 0.003 to 0.25% of the film thickness in a depth

direction of a surface layer of the substrate.

28. The battery separator for secondary cell according to any of the above items 25 through 27, wherein the surface layer comprises layers on both surfaces.

5 29. The battery separator for secondary cell according to any of the above items 25 through 28, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

In the case that the substrate is an assembly of fibers such as woven or nonwoven fabric, "the surface layer of the substrate" 10 means surface layer of the fiber which forms the substrate.

In the present invention, for the product produced by subjecting the substrate to the radical generation and the radical-induced chemical reaction, as means for measuring the atomic groups or some of the atoms constituting the introduced desired 15 substance in the depth direction from the surface of the product inwards, for example there are a total reflection measurement method using Fourier transform infrared spectroscopy in which measurement is carried out by changing the angle of incidence of the infrared rays, a method using a transmission electron microscope, and a method 20 using X-ray photoelectron spectroscopy. X-ray photoelectron spectroscopy is particularly suitable for analyzing the distribution of some of the atoms constituting the desired substance in a range of from 1 to 100 nm in the depth direction from the surface of the product inwards in the present invention. X-ray photoelectron 25 spectroscopy is a method in which, for example, in measurement on an organic polymer or the like, etching is carried out using Ar ions or the like so as to etch away the material from the surface, during which qualitative or quantitative information on atoms

present in the vicinity of the etching position can be obtained. For example, in the case of introducing sulfonic acid groups as functional atomic groups, measurement on the amount present of sulfur atoms contained in the sulfonic acid groups can be obtained by
5 irradiating X-rays in the depth direction from the surface of the product inwards, and measuring the energy of secondary electrons that are excited and thus jump out and the number of these secondary electrons at each energy, whereby the number of sulfur atoms present, or the state of bonding of these sulfur atoms to other atoms, in
10 a region from the surface inwards can be obtained. The results of such measurement can be compared with the required amount of functional atomic groups in accordance with the desired use, and thus used in product quality management.

Examples

15 Following is a more concrete description of the present invention through examples. The following description merely gives specific examples of the present invention, and the present invention is not limited thereby.

Example 1

20 The interior of a glove box as shown in FIG. 4 was put under a nitrogen atmosphere, the oxygen concentration was continuously measured using a galvanic cell type oxygen concentration meter (made by Iijima Electronics Corporation, model number MC7G-L) as oxygen concentration measuring means, and with the oxygen concentration
25 held in the range of more than 5 ppm and less than 30 ppm, 0.87 g (100 mm × 150 mm) of a poly(chlorotrifluoroethylene) resin film (Neoflon made by Daikin, mean film thickness 25 μ m, mean weight 55 g/m²) was put into a polyethylene bag. Next, the polyethylene

bag with the film therein was taken out from the glove box, and was irradiated with a 200 kGy electron beam. A mixed liquid of styrene monomer (70 ml) and toluene (30 ml) was aerated with nitrogen gas under an oxygen concentration of 10 ppm in the glove box for 30 minutes. The irradiated film and the aerated mixed liquid were then put into a glass vessel under an oxygen concentration in the range of more than 5 ppm and less than 10 ppm in the glove box, the glass vessel was sealed, and graft polymerization was carried out for 2 hours at 60°C. After that, the grafted film was taken out, removal of homopolymer was carried out for 2 hours using a Soxhlet extractor with acetone as an extraction solvent, and then drying was carried out for 30 minutes at 70°C, whereby 1.15 g of a styrene-grafted film was obtained. The graft rate as determined from the weight change was 32.2%.

The grafted film obtained was immersed in a mixed liquid of chlorosulfonic acid / dichloromethane in a weight ratio of 2 / 98, and sulfonation was carried out for 2 hours at 5°C. The film was then taken out, washed successively with a mixed liquid of methanol / dichloromethane in a weight ratio of 10 / 90, methanol, and then pure water, and then dried, whereby a sulfonated film A having an ion exchange capacity of 170 meq/m² was obtained.

Comparative Example 1

0.88 g (100 mm × 150 mm) of the same poly(chlorotrifluoroethylene) resin film as that used in Example 1 was put into a polyethylene bag under a nitrogen atmosphere with an oxygen concentration in the range of more than 10 ppm and less than 25 ppm in a glove box like that used in Example 1, and the polyethylene bag with the film therein was taken out from the glove

box, and was irradiated with a 200 kGy electron beam. The irradiated film, and a mixed liquid of styrene monomer (70 ml) and toluene (30 ml) that had been aerated with nitrogen gas for 30 minutes were then put into a glass vessel under an oxygen concentration in the range of more than 100 ppm and less than 110 ppm in the glove box, the glass vessel was sealed, and graft polymerization was carried out for 2 hours at 60° C. The grafted film was then taken out, removal of homopolymer was carried out for 2 hours using a Soxhlet extractor with acetone as an extraction solvent, and then drying was carried out for 30 minutes at 70° C, whereby 1.12 g of a styrene-grafted film was obtained. The graft rate as determined from the weight change was 27.3%.

The grafted film obtained was immersed in a mixed liquid of chlorosulfonic acid / dichloromethane in a weight ratio of 2 / 98, and sulfonation was carried out for 2 hours at 5° C. The film was then taken out, washed successively with a mixed liquid of methanol / dichloromethane in a weight ratio of 10 / 90, methanol, and then pure water, and then dried, whereby a sulfonated film B having an ion exchange capacity of 168 meq/m² was obtained.

Example 2

Using a continuous conveyance type reactor as shown in FIG. 1, a polyethylene fiber nonwoven fabric (made by DuPont-Asahi Flash Spun Products Co., Ltd., trade name Tyvek, mean fiber diameter 0.5 to 10 μ m, weight 65 g/m², thickness 0.17 mm, 300 mm wide $\times$ 200 m long roll) was subjected to an impregnation vapor phase graft polymerization reaction. Specifically, the interior of the irradiating chamber was put under a nitrogen atmosphere, the oxygen concentration was continuously measured using a galvanic cell type

oxygen concentration meter (made by Japan Air Gases Ltd., model number MKI-50) as oxygen concentration measuring means, and with the oxygen concentration held in the range of more than 25 ppm and less than 50 ppm, the nonwoven fabric was irradiated with a 150 kGy electron beam. Chloromethylstyrene (CMS-AM made by Seimi Chemical Co., Ltd.) was treated with basic alumina to adsorb and thus remove the polymerization inhibitor therein, and then toluene was added to prepare a chloromethylstyrene / toluene (weight ratio 80 / 20) solution, and after aerating with nitrogen for 30 minutes, the solution was introduced into the impregnator. While continuously measuring the oxygen concentration in the impregnator and the reactor using oxygen concentration meters (MC7G-L made by Iijima Electronics Corporation), with the oxygen concentration in the impregnator held in the range of more than 5 ppm and less than 15 ppm, and the oxygen concentration in the reactor held in the range of more than 15 ppm and less than 25 ppm, the irradiated nonwoven fabric obtained as described above was conveyed into the impregnator at a rate of 0.6 m/min and impregnated with the solution, and was then conveyed into the reactor and subjected to graft polymerization for 40 minutes at 60° C. Samples of size product width × 300 mm were cut out at three points at 80 m intervals in the length direction of the grafted nonwoven fabric thus manufactured (product length = 162 m), and the samples were treated for 3 hours at 60° C in toluene so as to remove homopolymer therefrom. The nonwoven fabric samples were then washed with acetone, and then dried for 2 hours at 60° C, whereby chloromethylstyrene-grafted nonwoven fabric samples were obtained. The graft rate as determined from the change in the weight of each of the samples obtained is shown in Table 1. The mean graft

rate was 47.6%.

Table 1

Position at which sample taken	Degree of grafting (%)
0 m	44.7
80 m	49.6
161 m	48.3
Average	47.6

Each of the chloromethylstyrene-grafted nonwoven fabric
5 samples obtained was immersed in a mixed liquid of isopropanol /
30% trimethylamine aqueous solution / pure water in a volume ratio
of 30 / 30 / 40, and reaction to form a quaternary ammonium salt
was carried out for 6 hours at 60°C. Each of the nonwoven fabric
samples was then taken out, washed three times with pure water at
10 40°C, and then dried for 1 hour at 50°C, whereby anion exchange
type nonwoven fabric samples C were obtained. The ion exchange
capacity of each of the nonwoven fabric samples C obtained is shown
in Table 2. The mean ion exchange capacity was 184 meq/m².

Table 2

Position at which sample taken	Ion exchange capacity (meq/m ²)
0 m	188
80 m	185
161 m	179
Average	184

15

Comparative Example 2

An impregnation vapor phase graft polymerization reaction
was carried out as in Example 2 using the same polyethylene fiber
nonwoven fabric as that used in Example 2. Specifically, with the
20 oxygen concentration in the irradiating chamber held at 250 ppm,
the nonwoven fabric was irradiated with a 150 kGy electron beam.

A purified chloromethylstyrene (CMS-AM made by Seimi Chemical Co., Ltd.) / toluene (weight ratio 80 / 20) solution was aerated with nitrogen for 30 minutes, and was then introduced into the impregnator. With the oxygen concentration in the impregnator held in the range of more than 5 ppm and less than 14 ppm, and the oxygen concentration in the reactor held in the range of more than 9 ppm and less than 37 ppm, the irradiated nonwoven fabric was conveyed into the impregnator at a rate of 0.6 m/min and impregnated with the solution, and was then conveyed into the reactor and subjected to graft polymerization for 40 minutes at 60° C. Samples of size product width × 300 mm were cut out at three points at 80 m intervals in the length direction of the grafted nonwoven fabric thus manufactured, and the samples were treated for 3 hours at 60° C in toluene so as to remove homopolymer therefrom. The nonwoven fabric samples were then washed with acetone, and then dried for 2 hours at 60° C, whereby chloromethylstyrene-grafted nonwoven fabric samples were obtained. The graft rate as determined from the change in the weight of each of the grafted nonwoven fabric samples obtained is shown in Table 3. The mean graft rate was 45.6%.

Table 3

Position at which sample taken	Degree of grafting (%)
0 m	46.1
80 m	46.6
160 m	44.1
Average	45.6

As in Example 2, each of the chloromethylstyrene-grafted nonwoven fabric samples obtained was immersed in a mixed liquid of isopropanol / 30% trimethylamine aqueous solution / pure water in a volume ratio of 30 / 30 / 40, and reaction to form a quaternary

ammonium salt was carried out for 6 hours at 60° C. Each of the nonwoven fabric samples was then taken out, washed three times with pure water at 40° C, and then dried for 1 hour at 50° C, whereby anion exchange type nonwoven fabric samples D were obtained. The ion exchange capacity of each of the nonwoven fabric samples D obtained is shown in Table 4. The mean ion exchange capacity was 176 meq/m².

Table 4

Position at which sample taken	Ion exchange capacity (meq/m ²)
0 m	192
80 m	172
161 m	163
Average	176

Example 3

The interior of a glove box as shown in FIG. 4 was put under a nitrogen atmosphere, the oxygen concentration was continuously measured using a galvanic cell type oxygen concentration meter (made by Iijima Electronics Corporation, model number MC7G-L) as oxygen concentration measuring means, and with the oxygen concentration held in the range of more than 5 ppm and less than 30 ppm, 3.94 g (200 mm × 300 mm) of a polyethylene fiber nonwoven fabric (made by DuPont-Asahi Flash Spun Products Co., Ltd., trade name Tyvek, mean fiber diameter 0.5 to 10 μm, weight 65 g/m², thickness 0.17 mm) was put into a polyethylene bag. The polyethylene bag with the nonwoven fabric therein was then taken out from the glove box, and was irradiated with a 150 kGy electron beam. A solution of lithium p-styrenesulfonate (made by Tosoh Corporation, trade name LiSS) in ethanol (weight ratio: 1/19) was aerated with nitrogen gas under an oxygen concentration of 10 ppm in the glove box for 30 minutes. The irradiated nonwoven fabric obtained as described above was

immersed in the aerated solution, then liquid was wiped off from the nonwoven fabric to make the total weight 7.80 g, and then the nonwoven fabric was put into a glass vessel under an oxygen concentration in the range of more than 5 ppm and less than 10 ppm in the glove box, the glass vessel was sealed, and graft polymerization was carried out for 3 hours at 60°C. After that, the grafted nonwoven fabric was taken out, removal of homopolymer was carried out by washing with pure water at 60°C, and then the water was wiped off, and drying was carried out for 1 hour at 50°C, whereby 4.22 g of a lithium styrenesulfonate-grafted nonwoven fabric was obtained. The graft rate as determined from the weight change was 7.1%.

The grafted nonwoven fabric obtained was washed twice with 0.5 mol/L hydrochloric acid (500 ml), and was then washed twice with pure water (500 ml) at 60°C, and then the water was wiped off, and drying was carried out for 1 hour at 50°C, whereby a 4.19 g cation exchange type nonwoven fabric E was obtained. The nonwoven fabric E obtained had an ion exchange capacity of 10.1 meq/m².

Comparative Example 3

3.89 g (200 mm × 300 mm) of a polyethylene fiber nonwoven fabric (made by DuPont-Asahi Flash Spun Products Co., Ltd., trade name Tyvek, mean fiber diameter 0.5 to 10 μm, weight 65 g/m², thickness 0.17 mm) was introduced into a polyethylene bag under a nitrogen atmosphere with an oxygen concentration in the range of more than 10 ppm and less than 25 ppm in a glove box like that used in Example 1, and the polyethylene bag with the nonwoven fabric therein was irradiated with a 150 kGy electron beam. The irradiated nonwoven fabric was then immersed in a solution of lithium p-styrenesulfonate

in ethanol (weight ratio: 1/19) that had been aerated with nitrogen gas for 30 minutes, then liquid was wiped off to make the total weight 7.80 g, and then the nonwoven fabric was put into a glass vessel under an oxygen concentration in the range of more than 100 ppm and less than 110 ppm in the same glove box used in Example 1, the glass vessel was sealed, and graft polymerization was carried out for 3 hours at 60° C. The grafted nonwoven fabric was then taken out, removal of homopolymer was carried out by washing with pure water at 60° C, and then the water was wiped off, and drying was carried out for 1 hour at 50° C, whereby 4.16 g of a lithium styrenesulfonate-grafted nonwoven fabric was obtained. The graft rate as determined from the weight change was 6.9%.

The grafted nonwoven fabric obtained was washed twice with 0.5 mol/L hydrochloric acid (500 ml), and was then washed twice with pure water (500 ml) at 60° C, and then the water was wiped off, and drying was carried out for 1 hour at 50° C, whereby a 4.13 g cation exchange type nonwoven fabric F was obtained. The nonwoven fabric F obtained had an ion exchange capacity of 9.8 meq/m².

Example 4

The sulfonated film A produced in Example 1, and the sulfonated film B produced in Comparative Example 1 were each subjected to measurement of the elemental distribution on the surface thereof using XPS.

Specifically, the surface of each film was washed with acetone, and was then irradiated with the K α line of Al (1,486.6 eV) as incident X rays in an elliptical shape approximately of major diameter 200 μ m and width 20 to 30 μ m. Photoelectrons thus generated were measured with a wide scan, and the elemental content in atom % in a 10 nm

depth range from the surface was determined. As a result, it was found that the abundance of S for sulfonated film A was 1 to 2 atom %. On the other hand, a response due to S was not detected for sulfonated film B.

5 Example 5

Sulfonated films A and B obtained in Example 1 and Comparative Example 1 and Nafion (Trademark) N115 made by DuPont were subjected to measurement of the voltage under a constant current using an ion conductivity measuring apparatus as shown in FIG. 5, whereby
10 the ion conductivity was measured. The results are shown in FIG. 6 as a graph in which the horizontal axis shows the current, and the vertical axis shows the voltage required under the constant current, which indicates the ion conductivity. From these results, it can be seen that the ion conductivity is better if the oxygen
15 concentration during the reaction is lower.

Example 6

Eight 4 mm × 25 mm strips were cut out from each of the anion exchange type nonwoven fabrics C and D obtained in Example 2 and Comparative Example 2, and the cation exchange type nonwoven fabrics
20 E and F obtained in Example 3 and Comparative Example 3. Next, the strips were immersed in pure water and thus washed, and then the water was wiped off, and drying was carried out for 2 hours at 50° C in a hot air drier. Using a water absorption rate measurement method as illustrated in FIG. 7, pure water was put into a channel of depth
25 1 mm, each of the samples taken out from the drier was immediately stood up such that the long sides thereof were vertical and the lower end thereof was placed in the channel, and then the change over time in the height reached by the pure water was measured.

Note that the room temperature was 25° C, and the relative humidity was 55%. The mean values of the results are shown in Table 5. Note that there were no samples at all of the aerobic treatment nonwoven fabric D for which the pure water was absorbed 10 mm or more. From the above, it was found that by controlling the oxygen concentration to be low during the electron beam irradiation, an ion exchange type nonwoven fabric having a high pure water absorption rate can be obtained.

Table 5: Time taken for pure water to be absorbed (s)

Height (mm)	Anion Exchange Type Nonwoven fabric C	Anion Exchange Type Nonwoven fabric D	Cation Exchange Type Nonwoven fabric E	Cation Exchange Type nonwoven fabric F
5	14	67	11	53
10	45	--	39	195
15	112	--	102 .	--

Example 7

FIG. 2 is a flowchart of an oxygen concentration control method, and FIG. 3 is a conceptual drawing of an example of application of this method to a continuous conveyance type grafting reaction apparatus. Using this apparatus, test operation was carried out with an oxygen concentration set value of 200 ppm on the irradiating device side and 50 ppm on the reactor side. Commencement of operation was not possible if either of these set values was exceeded, trial operation was commenced once the oxygen concentration was below the set values, and if the oxygen concentration rose, then a warning was issued by means of a buzzer and a Patlite (registered trademark) coming on, and a warning message was displayed on a control console touch panel. In this case, the irradiation was stopped, and then conveyance was stopped.

CLAIMS

1. An organic polymeric material comprising a chemically modified organic polymeric material substrate, wherein a response
5 due to the chemical modification is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

2. An organic polymeric material according to claim 1, wherein a region of from 1 ppm to 100 nm in a depth direction of a surface layer of the substrate is chemically modified.

10 3. The organic polymeric material according to claim 1 or 2, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

4. The organic polymeric material according to any of claims 1 to 3, wherein the organic polymeric material is a film-shaped
15 organic polymeric material comprising a chemically modified film-shaped organic polymeric material substrate.

5. The film-shaped organic polymeric material comprising a chemically modified film-shaped organic polymeric material substrate according to claim 4, wherein a region of from 0.02 %
20 to 0.5% of the film thickness in a depth direction of a surface layer of the substrate is chemically modified.

6. The organic polymeric material according to claim 4 or 5, wherein the surface layer comprises layers on both surfaces.

7. The organic polymeric material according to any of
25 claims 4 through 6, wherein the film-shaped substrate comprises a polyolefin and/or a halogenated polyolefin.

8. An organic polymeric material comprising a fiber or an assembly of fibers obtained by chemically modifying an organic

polymeric material substrate having the form of a fiber or an assembly of fibers, wherein a response due to the chemical modification is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

5 9. The organic polymeric material according to claim 8, wherein a region of from 1 nm to 100 nm in a depth direction of a surface layer of the fibrous substrate is chemically modified.

10 10. The organic polymeric material comprising a fiber or an assembly of fibers obtained by chemically modifying an organic polymeric material substrate having the form of a fiber or an assembly of fibers according to claim 8 or 9, wherein from 0.02 % to 0.5% of the fiber diameter in a depth direction of a surface layer of the fibrous substrate is chemically modified.

15 11. The organic polymeric material according to any of claims 8 to 10, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

20 12. The organic polymeric material according to any of claims 1 through 11, wherein in the chemically modified organic polymeric material, the chemical modification includes a radical-induced chemical reaction.

 13. The organic polymeric material according to claim 12, wherein means for generating the radicals is irradiation with ionizing radiation.

25 14. The organic polymeric material according to any of claims 12 or 13, wherein the radical-induced chemical reaction is graft polymerization.

 15. The organic polymeric material according to claim 14, wherein grafted side chains introduced onto the substrate through

the graft polymerization are further chemically modified.

16. The organic polymeric material according to any of claims 1 through 15, wherein in the chemically modified organic polymeric material, the chemical modification comprises
5 introduction of ion exchange groups.

17. The organic polymeric material according to any of claims 1 through 15, wherein in the chemically modified organic polymeric material, the chemical modification comprises
introduction of ligands.

10 18. An electrolyte film comprising the organic polymeric material according to any of claims 1 through 16 obtained by introducing ion exchange groups onto the organic polymeric material substrate, wherein the ion exchange groups are introduced through reaction including a radical-induced chemical reaction.

15 19. An electrolyte film comprising an organic polymeric material substrate having ion exchange groups introduced thereon, wherein a response due to the introduction of the ion exchange groups is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

20 20. The electrolyte film according to claim 19, wherein the ion exchange groups are introduced in a region of from 1 nm to 10 nm in a depth direction of a surface layer of the substrate.

21. An electrolyte film comprising an organic polymeric material substrate having ion exchange groups introduced thereon
25 according to claim 19 or 20, wherein the ion exchange groups are introduced in a region of from 0.003 % to 0.05% of the film thickness in a depth direction of a surface layer of the substrate.

22. The electrolyte film according to any of claims 19

through 21, wherein the surface layer comprises layers on both surfaces.

23. The electrolyte film according to any of claims 19 through 22, wherein the substrate comprises a polyolefin and/or
5 a halogenated polyolefin.

24. A battery separator for secondary cell comprising the organic polymeric material according to any of claims 1 through 16 obtained by introducing ion exchange groups onto the organic polymeric material substrate, wherein the ion exchange groups are
10 introduced through reaction including a radical-induced chemical reaction.

25. A battery separator for secondary cell comprising an organic polymeric material substrate having ion exchange groups introduced thereon, wherein a response due to the introduction of
15 the ion exchange groups is detected by X-ray photoelectron spectroscopy (XPS) for a surface layer of the substrate.

26. The battery separator for secondary cell according to claim 25, wherein the ion exchange groups are introduced in a region of from 1 nm to 50 nm in a depth direction of a surface layer of
20 the substrate.

27. A battery separator for secondary cell according to claim 25, wherein the ion exchange groups are introduced in a region of from 0.003 % to 0.25% of the film thickness in a depth direction of a surface layer of the substrate.

28. The battery separator for secondary cell according to any of claims 25 through 27, wherein the surface layer comprises layers on both surfaces.

29. The battery separator for secondary cell according to

any of claims 25 through 28, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

30. A method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate, which comprises putting the substrate into a container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, generating radicals on the substrate in part of the container, and then moving the substrate into another part of the container, and chemically modifying the substrate through a radical-induced reaction, and wherein the oxygen concentration of the atmosphere in which the chemical modification is carried out is in a range of from 1 ppm to 100 ppm.

31. A method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate, wherein the method comprises putting the substrate into a container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, generating radicals on the substrate in part of the container, and then moving the substrate into another part of the container, and chemically modifying the substrate through a radical-induced reaction, and wherein the oxygen concentration of the atmosphere in which the radicals are generated is in a range of from 1 ppm to 200 ppm.

32. A method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate, wherein the method comprises putting the substrate into a container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, generating

radicals on the substrate in part of the container, and then moving the substrate into another part of the container, and chemically modifying the substrate through a radical-induced reaction, and wherein the oxygen concentration of the atmosphere in which the chemical modification is carried out is in a range of from 1 ppm to 100 ppm, and the oxygen concentration of the atmosphere in which the radicals are generated is in a range of from 1 ppm to 200 ppm.

33. The method of manufacturing an organic polymeric material according to any of claims 30 through 32, wherein the container is a container partitioned into a portion in which the radicals are generated on the substrate and a portion in which the chemical modification is carried out.

34. The method of manufacturing an organic polymeric material according to any of claims 30 through 32, wherein the container comprises a container in which the radicals are generated on the substrate and a separate container in which the chemical modification is carried out, and the method further comprises moving the substrate from the container in which the radicals are generated to the container in which the chemical modification is carried out via a connecting section that is isolated from the outside environment and through which the substrate can be moved while holding the oxygen concentration of the atmosphere therein in a range of from 1 ppm to 100 ppm.

35. A method of manufacturing an organic polymeric material by chemically modifying an organic polymeric material substrate, wherein the method comprises putting the substrate into a container that can be isolated from the outside environment and in which the oxygen concentration can be held lower than that outside, and

generating radicals on the substrate while bringing the substrate and a reactant for the chemical modification into contact with one another in part of the container, and wherein the oxygen concentration of the atmosphere in which the chemical modification is carried out is in a range of from 1 ppm to 100 ppm.

36. The method of manufacturing an organic polymeric material according to any of claims 30 through 35, wherein means for generating the radicals is irradiation with ionizing radiation.

37. The method of manufacturing an organic polymeric material according to any of claims 30 through 36, wherein the chemical modification includes graft polymerization.

38. The method of manufacturing an organic polymeric material according to any of claims 30 through 37, wherein the substrate comprises a polyolefin and/or a halogenated polyolefin.

39. The method of manufacturing an organic polymeric material according to any of claims 30 through 38, wherein the substrate is a sheet-shaped material of a fiber aggregate or a film, and at least one selected from a step of supplying the substrate into a space in which the reaction is carried out, a step of generating the radicals on the substrate, a step of carrying out the chemical modification on the substrate, and a step of conveying a product out is carried out continuously.

40. The method of manufacturing an organic polymeric material according to any of claims 30 through 39, wherein the oxygen concentration in the space in which the reaction is carried out is held lower than that outside by supplying an inert gas having an oxygen concentration in a range of from 1 ppb to 100 ppm into the space in which the reaction is carried out so as to replace

gas in the space in which the reaction is carried out.

41. The method of manufacturing an organic polymeric material according to any of claims 30 through 40, wherein the oxygen concentration in the space in which the reaction is carried out is held lower than that outside by supplying an inert gas having an oxygen concentration in a range of from 0.1 ppm to 100 ppm into the space in which the reaction is carried out, exhausting gas from the space in which the reaction is carried out and subjecting the gas to deoxygenation treatment, and then returning the gas into the space in which the reaction is carried out, thus carrying out circulation and replacement of the gas in the space in which the reaction is carried out.

42. The method of manufacturing an organic polymeric material according to claim 40 or 41, wherein the inert gas is nitrogen gas of purity not less than 99.99%.

43. A method of inspecting a film-shaped organic polymeric material obtained by chemically modifying an organic polymeric material substrate, the method comprising measuring by X-ray photoelectron spectroscopy (XPS) that a region of from 1 nm to 100 nm in a depth direction of a surface layer of the manufactured film-shaped organic polymeric material is chemically modified.

44. An organic polymeric material chemical modification apparatus for manufacturing a film-shaped organic polymeric material by chemically modifying an organic polymeric material substrate, the apparatus comprising:

an ionizing radiation irradiating section that is disposed in a first container that isolates the substrate from the outside environment and in which the oxygen concentration can be held lower

than that outside, and is for generating radicals on the organic polymeric material substrate;

a chemical modification section that is disposed in a second container that isolates the substrate from the outside environment
5 and in which the oxygen concentration can be held lower than that outside, and is for carrying out chemical modification through a reaction induced by the radicals; and

a connecting section that is disposed in a third container that isolates the substrate from the outside environment and in
10 which the oxygen concentration can be held lower than that outside, and connects the container in which the ionizing radiation irradiating section is disposed to the container in which the chemical modification section is disposed, enabling the substrate to be moved therebetween, wherein

15 one of the first container in which the ionizing radiation irradiating section is disposed, the second container in which the chemical modification section is disposed, and the third container in which the connecting section is disposed is provided with at least one inert gas supply port for supplying an inert gas into
20 the container, and at least one exhaust port for exhausting gas from the container, and wherein

the apparatus further comprises a mechanism to hold the oxygen concentration of the gas in the first container in which the ionizing radiation irradiating section is disposed in a range of from 0.1
25 ppm to 200 ppm, and/or the oxygen concentration of the gas in the second container in which the chemical modification section is disposed is held in a range of from 0.1 ppm to 100 ppm.

45. An organic polymeric material chemical modification

apparatus for manufacturing a film-shaped organic polymeric material by chemically modifying an organic polymeric material substrate, the apparatus comprising:

5 a container that isolates the substrate from the outside environment and in which the oxygen concentration can be held lower than that outside;

an ionizing radiation irradiating section that is disposed in the container, and is for generating radicals on the organic polymeric material substrate;

10 a chemical modification section that is disposed in the container, and is for chemically modifying the substrate through a reaction induced by the radicals; and

a conveyance section that is disposed in the container, and is for conveying the substrate from the ionizing radiation
15 irradiating section into the chemical modification section, wherein

the container is provided with an inert gas supply port for supplying an inert gas into the container, and an exhaust port for exhausting gas from the container, and wherein

the apparatus further comprises a mechanism to hold the oxygen
20 concentration of the gas in the container in a range of from 0.1 ppm to 100 ppm.

46. The organic polymeric material chemical modification apparatus according to claim 44 or 45, further comprising an oxygen concentration meter that continuously monitors the oxygen
25 concentration of the gas in the ionizing radiation irradiating section and/or the chemical modification section, and further comprising a warning device for issuing a warning if the oxygen concentration deviates from a prescribed concentration range.

47. The organic polymeric material chemical modification apparatus according to any of claims 44 through 46, comprising an oxygen concentration meter that continuously monitors the oxygen concentration of the gas in the ionizing radiation irradiating section and/or the chemical modification section, and further comprising a shutdown device for stopping the irradiation with the ionizing radiation and/or stopping the chemical modification reaction if the oxygen concentration deviates from a prescribed concentration range.

48. The organic polymeric material chemical modification apparatus according to any of claims 44 through 47, comprising an oxygen concentration meter that monitors the oxygen concentration of the gas in the ionizing radiation irradiating section and/or the chemical modification section, and further comprising a control device for controlling commencement of operation of the apparatus to be operational when the oxygen concentration of the gas in each of the ionizing radiation irradiating section and the chemical modification section is within a prescribed concentration range.

49. A computer-readable apparatus operation program for the organic polymeric material chemical modification apparatus according to any of claims 44 through 48, for implementing a step of making the oxygen concentration of the gas in each of the ionizing radiation irradiating section, the chemical modification section and the connecting section be within a prescribed concentration range by replacing the gas in each of the ionizing radiation irradiating section, the chemical modification section and the connecting section with an inert gas in which the oxygen concentration is within a prescribed concentration range, a step of moving a

substrate that has been conveyed in from a substrate supply section into the ionizing radiation irradiating section, and irradiating the substrate with a prescribed amount of ionizing radiation by adjusting an irradiation source and the irradiation time, thus
5 generating radicals on the substrate, a step of moving the substrate on which the radicals have been generated into the chemical modification section, bringing the substrate into contact with a prescribed reactant containing a chemical species required in chemical modification induced by the radicals, and carrying out
10 the chemical modification at a prescribed reaction temperature for a prescribed reaction time, thus producing a chemically modified product, and a step of conveying the chemically modified product out using a product conveying section.

15

Fig. 1

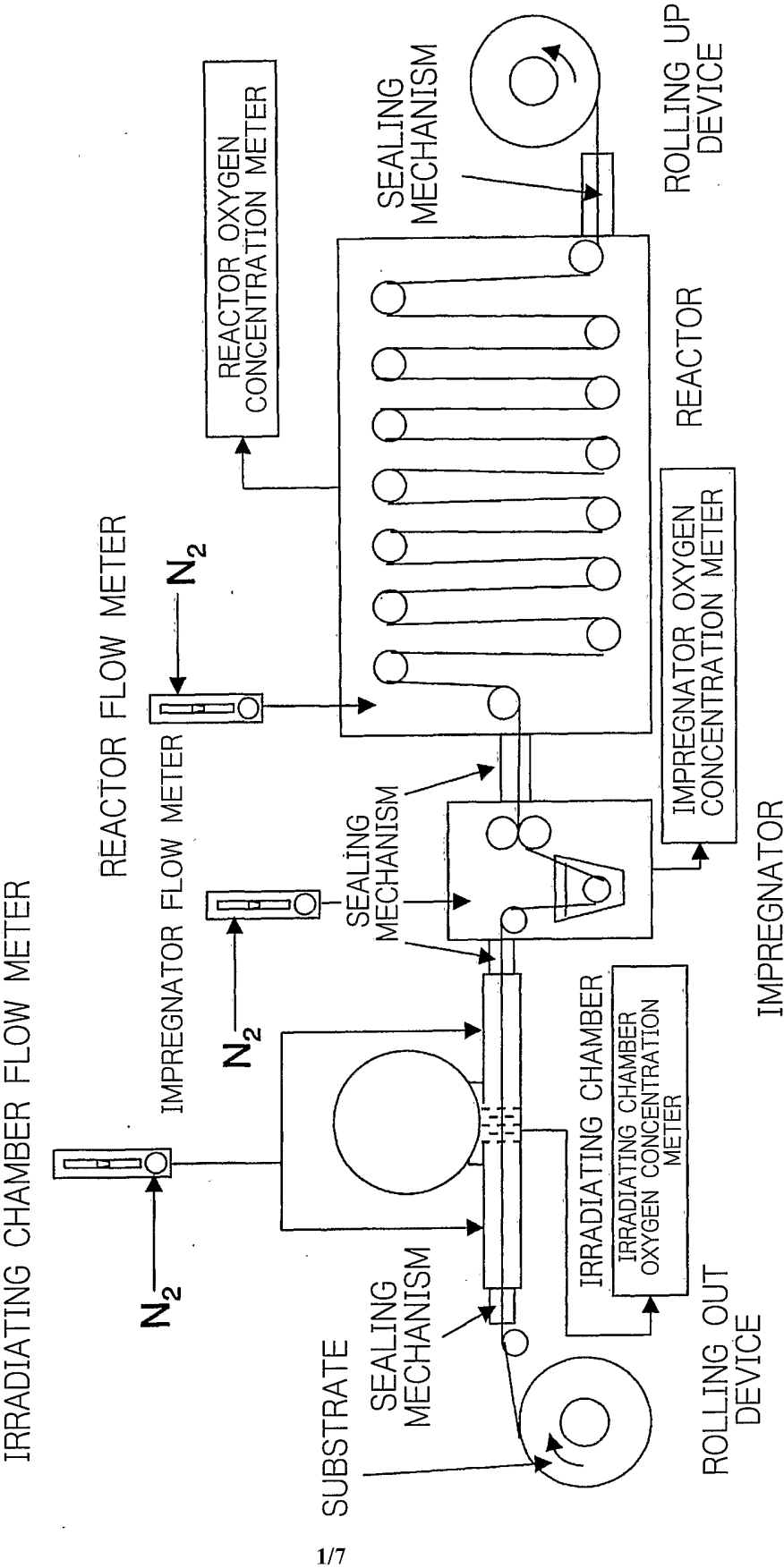


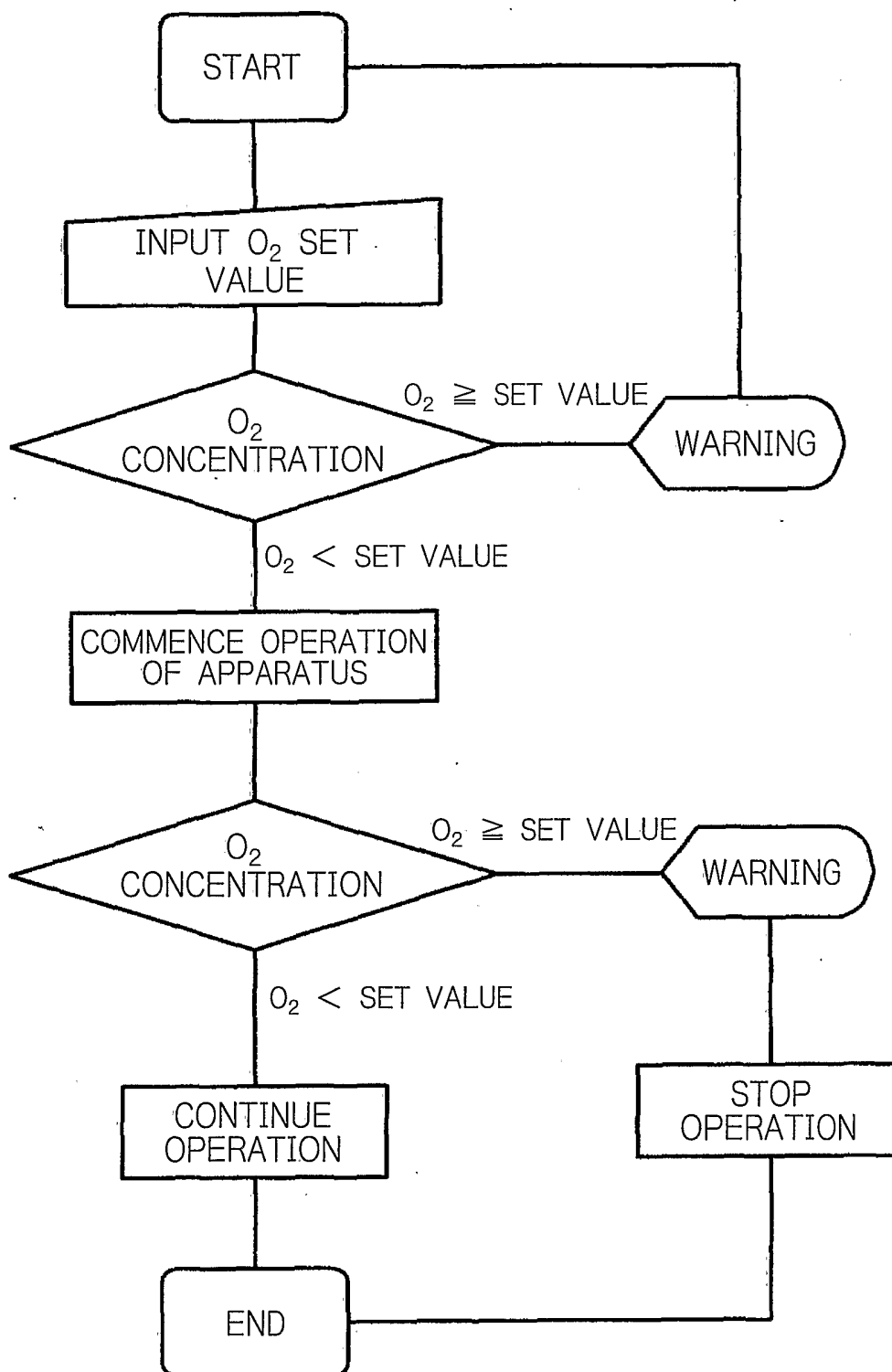
Fig. 2

Fig. 3

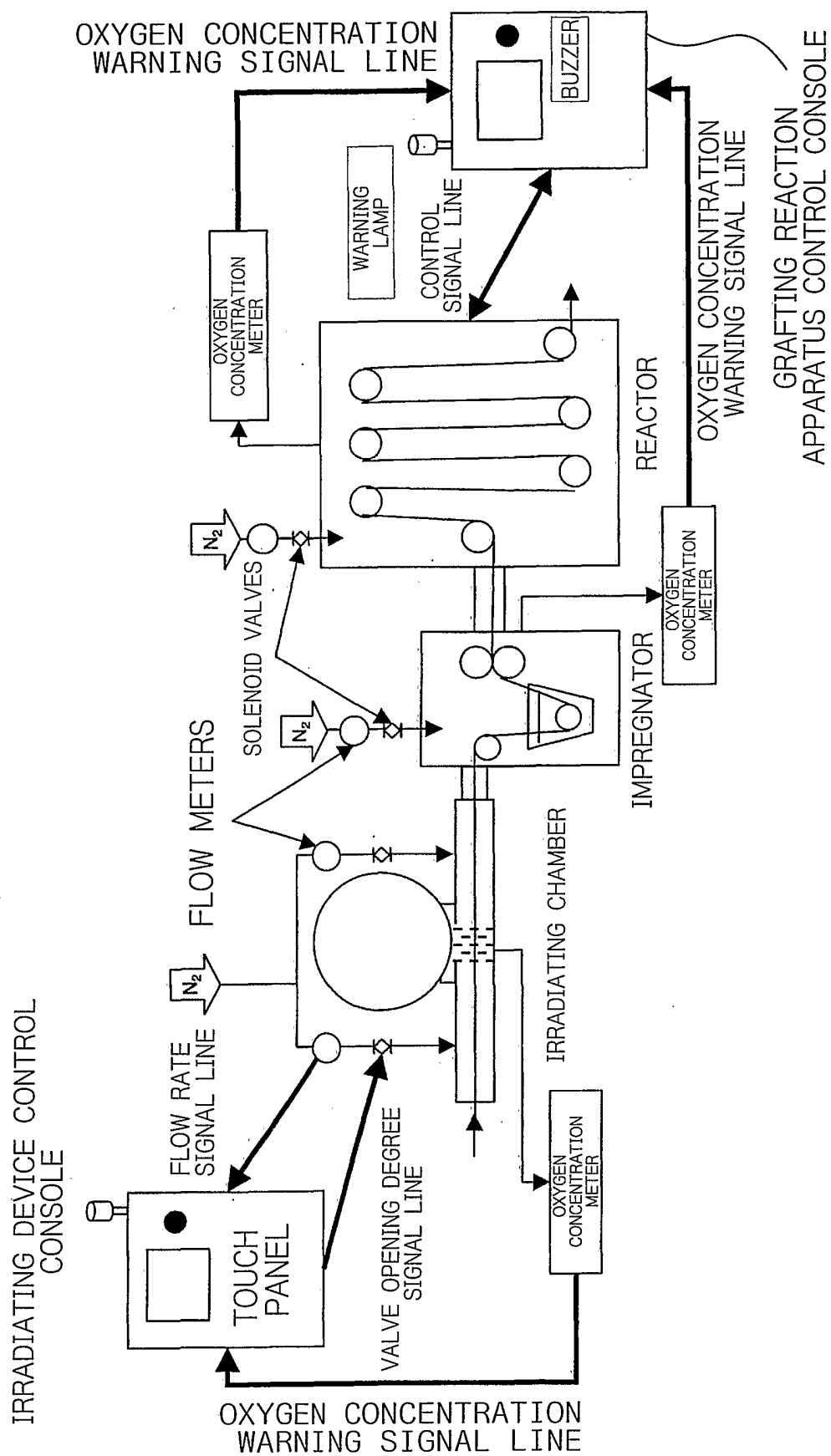


Fig. 4

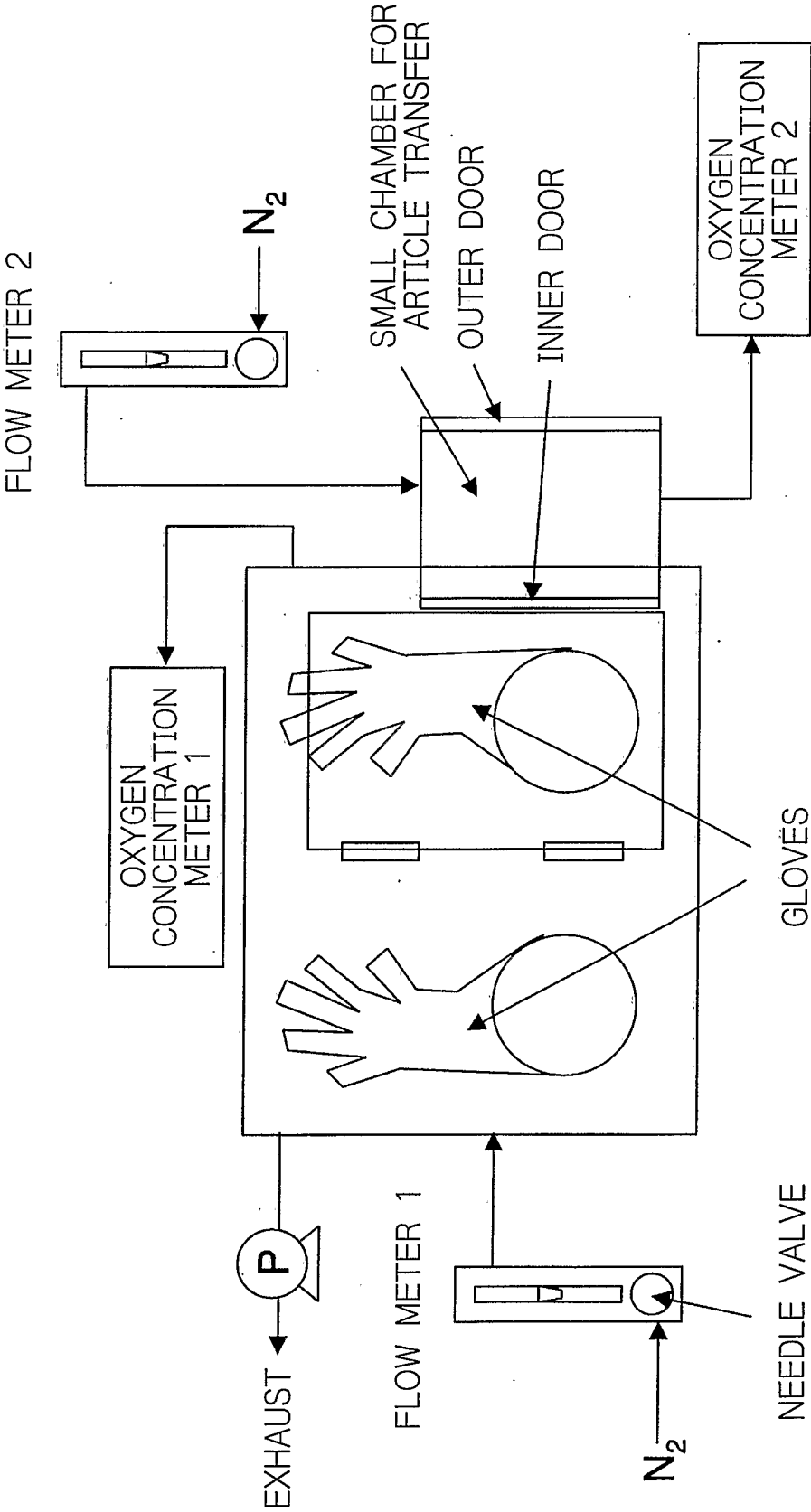


Fig. 5

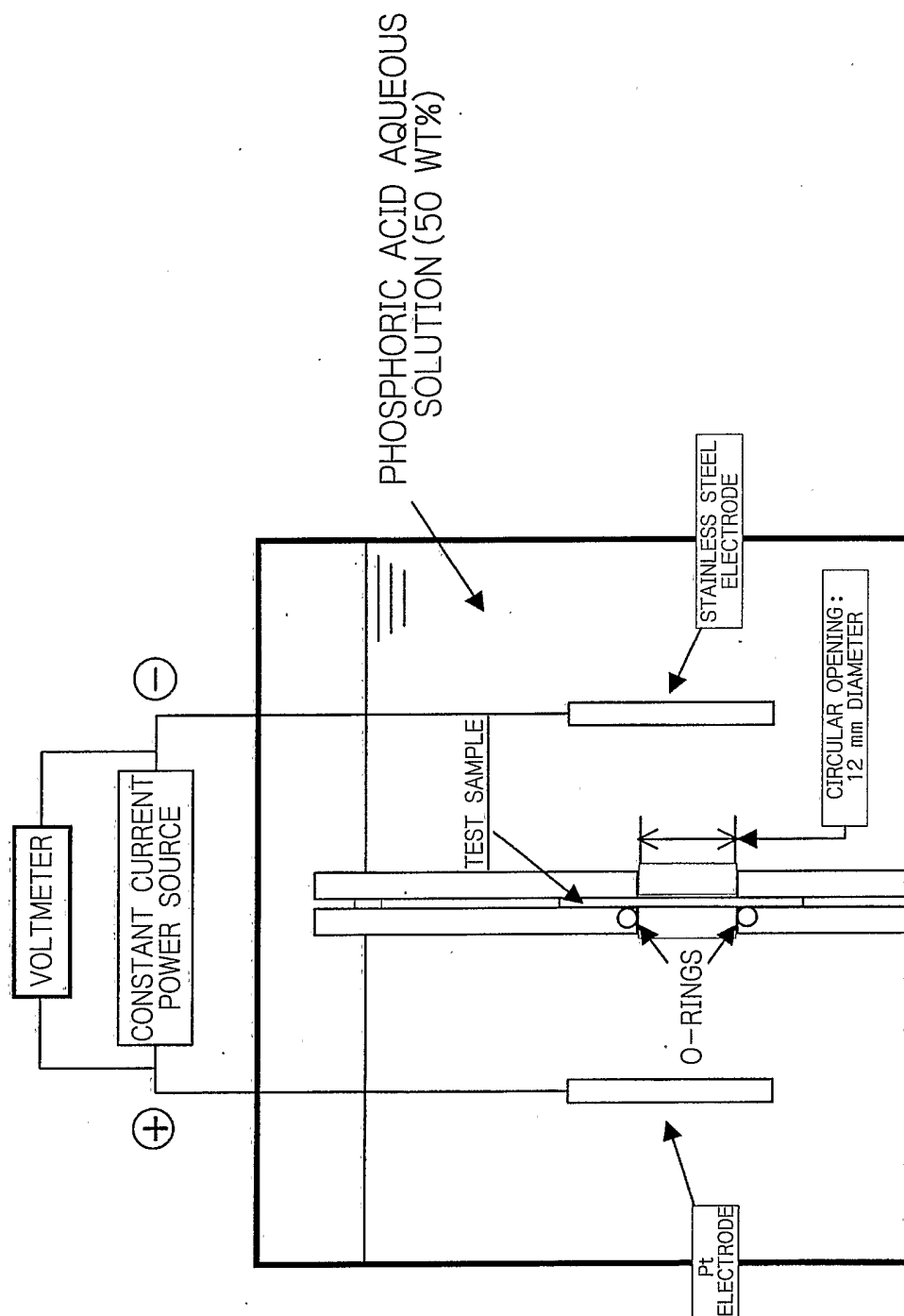


Fig. 6

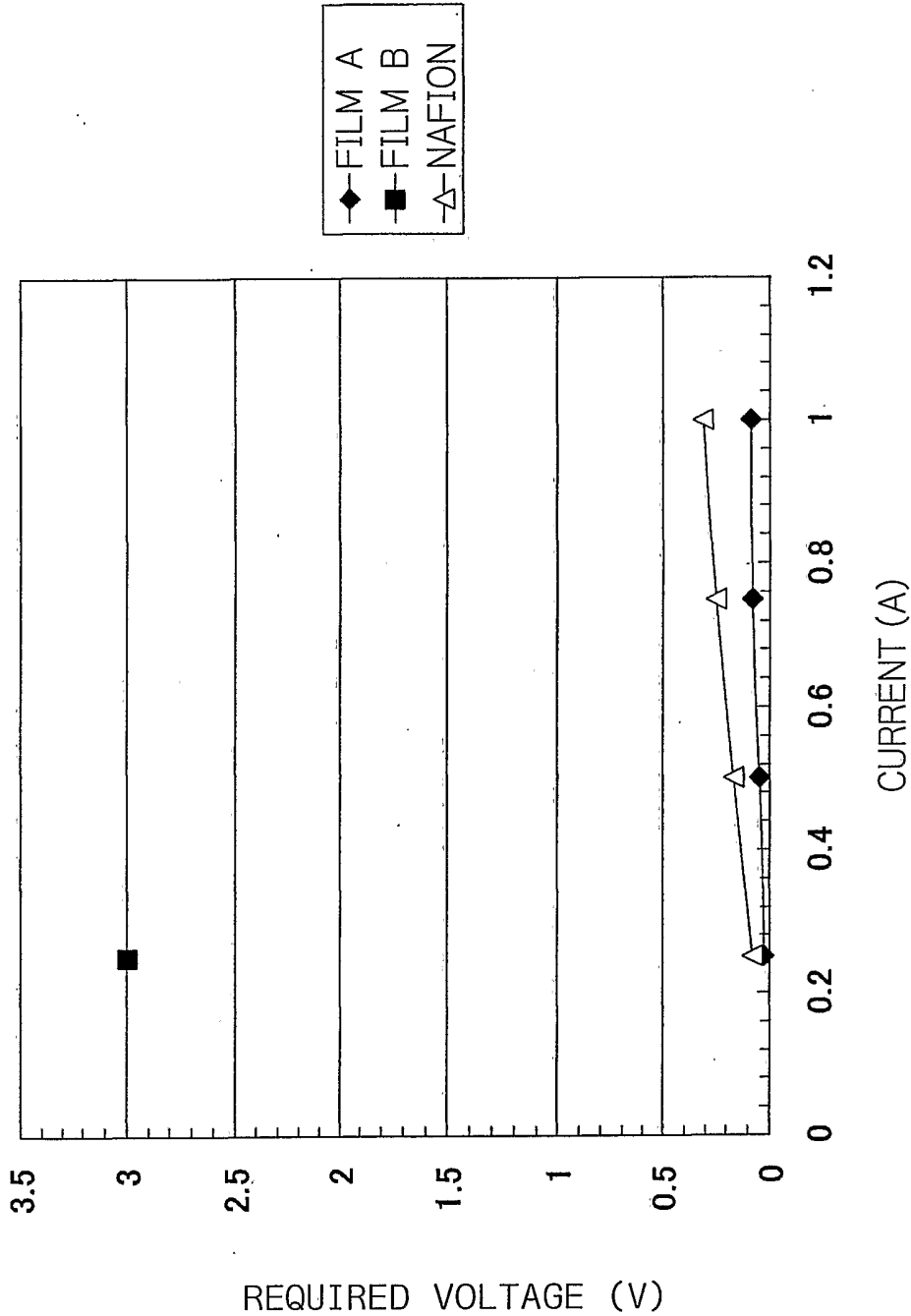


Fig. 7

