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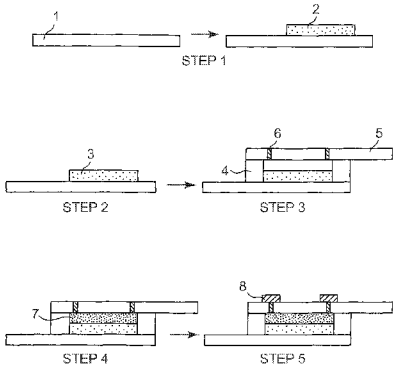

Fig. 1

(57) Abstract: An electrolyte solution for dye-sensitized solar cells being capable to have a high photoelectric conversion efficiency and to be almost colorless and transparent, are provided by using an electrolyte solution for dye-sensitized solar cells. The electrolyte solution comprising a halide salt formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide. The concentration of halogen molecules in the electrolyte solution is in the range of 0 to 0.0004 moles/liter.

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AN ELECTROLYTE SOLUTION FOR DYE-SENSITIZED SOLAR CELLS AND A DYE-SENSITIZED SOLAR CELL

TECHNICAL FIELD

The present invention relates to a dye-sensitized solar cell and to an electrolyte solution for dye-sensitized solar cells that is capable of being almost colorless and transparent.

BACKGROUND

Dye-sensitized solar cells are being developed as the next generation solar cells. Since dye-sensitized solar cells obviate the need for battery exchange and a feeder line, these solar cells can be used in a variety of applications including those where enhanced convenience is desired and those where providing an electric supply is difficult. Dye-sensitized solar cells and electrolyte solutions used therefore are described in the following references.

Japanese Unexamined Patent Publication (Kokai) No. 1-220380 describes a regenerative-type photoelectrochemical battery that has a semiconductor made of the polycrystalline metal oxide and that has a mono-molecular color-developing agent layer of phthalocyanine, porphyrin or the like throughout the surface region. As the electrolyte, the redox system of an iodide, a bromide, hydroquinone, or the like can be used.

PCT Application Publication WO 95/18456 describes a regenerative-type photoelectrochemical battery that has as an electrolyte solution this is an oxidation-reduction system. This system includes a mixture of at least one electrochemically active salt and at least one type of molecules designed to form an oxidation-reduction system with an anion or a cation of the active salt. The oxidation-reduction system is a liquid at room temperature and a solution in an electrochemically inactive salt having a melting point below room temperature.

Japanese Patent Publication No. 2008-16442 describes a photoelectric conversion element wherein the electrolyte layer does not contain an iodine compound but contains an organic or inorganic cation and an aromatic or heteroaromatic cyclic compound such as a thiadiazole compound or a pyridine compound.

Japanese Patent Publication No. 2000-277182(A) describes a non-aqueous electrolyte solution for dye-sensitized solar cells. The electrolyte solution contains a non-aqueous solvent, iodine or the like, and a quaternary salt of a cyclic amidine compound having a 2-imidazoline ring.

Japanese Unexamined Patent Publication (Kokai) No. 2005-172722 describes a

film-forming composition that contains 10-35% by weight of crystalline semiconductor nanoparticles, 0.2-5% by weight of a binder and a mixture of an alcohol having 3-5 carbons and water with a water content of 20-60% by weight. The composition can be used in a film-type dye-sensitized light intensity conversion element having a viscosity of at least 2.5 Pa·s.

SUMMARY OF THE INVENTION

Among the known electrolyte solutions for dye-sensitized solar cells, electrolyte solutions containing a halogen molecule and a halide salt such as I_2 and an iodide salt as the oxidation-reduction pair have excellent photoelectric conversion efficiency. However, since halogen molecules such as iodine (I_2) and bromine (Br_2) are colored (e.g., red brown) in a solvent, a dye-sensitized solar cell that employs the above electrolyte solution is colored. Such dye-sensitized solar cells tend to have poor light transmission and color limitations. Therefore, there is a need for an electrolyte solution for dye-sensitized solar cells that are transparent in the visible region while maintaining suitable photoelectric conversion characteristics. Likewise, there is a need for dye-sensitized solar cells that contain such electrolyte solutions.

In accordance with the present invention, it was found, the above problem can be solved by using an electrolyte solution for dye-sensitized solar cells that contains a halide salt formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide ion. The electrolyte solutions often contain no halogen molecules or contain no greater than 0.0004 moles/liter halogen molecules.

In accordance with an embodiment of the present invention, dye-sensitized solar cells are provided that contain the above described electrolyte solution.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a drawing that shows a production scheme for a dye-sensitized solar cell.

Fig. 2 is a graph that shows light transmission efficiency at 300-800 nm of electrolyte solutions of Working Examples 7 to 10 and Comparative Example 2.

DETAILED DESCRIPTION OF THE INVENTION

An electrolyte solution for dye-sensitized solar cells is provided by an embodiment of the present invention that contains a maximum of 0.0004 moles/liter of a halogen molecule such as I_2 and Br_2. These electrolyte solutions have high light transmission in the entire region of the visible light. The electrolyte solutions can be rendered almost

colorless and transparent in the visible wavelength region of the electromagnetic spectrum. Being colorless and transparent, these electrolyte solutions enable a wide variety of designs for the solar cells. Also, since the electrolyte solutions contain halogen molecule such as I_2 and Br_2 in an amount in the range of 0 to 0.0004 moles/liter, the electrolyte solutions undergo little deterioration of their performance characteristics under the sunlight, have excellent anti-cycle durability, and have very low corrosiveness. A wide assortment of substrates can be used with the electrolyte solution such as, for example, a metal plate. The electrolyte solutions have photoelectric conversion efficiencies, open voltage values, short-circuit current values, fill factors, and the like comparable to those of conventional electrolyte solutions containing I_2 or higher concentrations of I_2.

A dye-sensitized solar cell is a solar cell that has a substrate, a photo anode comprising a porous semiconductor metal oxide such as a dye-adsorbed ITO, a counter electrode, an electrolyte solution and the like, and that generates electricity by a photoelectric conversion effect when exposed to light such as a visible light. The electrolyte solution as claimed in the present invention may be used in such a dye-sensitized solar cell.

An electrolyte solution for dye-sensitized solar cells of the present invention comprises a halide salt formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide ion. The electrolyte solution contains no halogen molecules or, if halogen molecules are present, the concentration is 0.0004 moles/liter or less. That is, electrolyte solution contains halogen molecules in the concentration range of 0 to 0.004 moles/liter.

In the electrolyte solution for dye-sensitized solar cells of the present invention, the concentration of a halogen molecule is defined by the concentration of the halogen molecule added as a raw material. Since the concentration of a halogen molecule such as I_2 and Br_2 is 0.0004 moles/liter or less (including zero), the electrolyte solution is capable of being almost colorless and transparent in the visible range, thereby contributing to a good light transmission, a high light conversion efficiency, an aesthetic appearance, and the like. The concentration of a halogen molecule in the electrolyte solution for dye-sensitized solar cells of the present invention may be 0.0004 moles/liter or less, and, as needed, may be in the range of 0 to 0.0002 moles/liter, in the range of 0 to 0.0001 moles/liter, or in the range of 0 to 0.00005 moles/liter. In some embodiments, no halogen molecules are added as a raw material.

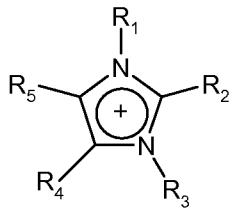
As used herein, to be colorless and transparent means that the transmission of the visible light at wavelengths of 380 to 780 nm in the visible range may be 60% or higher,

and more preferably 85% or higher. In accordance with the present invention, the transmission of the visible light may be 90% or higher, 95% or higher, 96% or higher, and further 98% or higher.

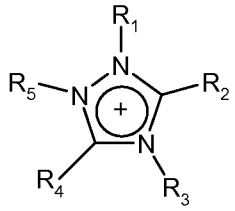
The electrolyte to be used in the electrolyte solution for the dye-sensitized solar cell according to one embodiment of the present invention comprises a halide salt formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide ion group.

Herein, the term quaternary nitrogen atom refers to a nitrogen atom having four hydrocarbon groups bonded to the nitrogen atom by way of C-N bonding, wherein the hydrocarbon groups may contain hetero atoms such as nitrogen atoms or oxygen atoms, etc., and may be saturated or unsaturated including the C-N bond, substituted or non-substituted, aliphatic or aromatic, or branched or linear, and may have various substituent groups on the hydrocarbon groups. A nitrogen atom included in an aromatic ring can be considered to be a quaternary nitrogen atom. That is, a nitrogen heteroatom in an aromatic ring can be considered to be a quaternary nitrogen atom even though there are only three groups attached to the nitrogen but one of these includes a double bond. Quaternary phosphorous atoms are similarly defined in which four hydrocarbon groups are bonded to the phosphorous atom by way of C-P bonding. Tertiary sulfur atom refers are similarly defined in which three hydrocarbon groups are bonded to the sulfur atom by way of C-S bonding.

The cation group comprising one or more groups containing at least one quaternary nitrogen atom may be an imidazolium-type group or a triazolium-type group represented by the following general Formulas (Ia) and (Ib). In these embodiments, the quaternary nitrogen is a heteroatom in an aromatic ring.



(Ia)

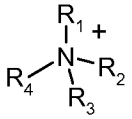


(Ib)

In Formula (Ia), each group R_1 and R_3 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, or (i) a polyether group. Each group R_2, R_4 and R_5 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, (i) a polyether group, or (j) hydrogen.

In Formula (Ib), each group R_1, R_3, and R_5 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, or (i) a polyether group. Each group R_2 and R_4 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, (i) a polyether group, or (j) hydrogen.

Alternatively, the cation group comprising one or more groups containing at least one quaternary atom may be an ammonium group represented by the general Formula (II).

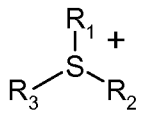


(II)

In Formula (II), each group R_1, R_2, R_3, and R_4 is independently selected from (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an

alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h), an alkoxy alkyl group, or (i) a polyether group. Some exemplary cation groups of Formula (III) are tetralkylammonium ions such as tetrabutylammonium.

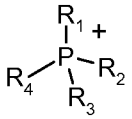
The cation group comprising one or more groups containing at least one tertiary sulfur atom may be a sulfonium group represented by the following general Formula III.



(III)

In Formula (III), each group R_1, R_2, and R_3 is independently selected from (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h), an alkoxy alkyl group, or (i) a polyether group.

The cation comprising one or more groups containing at least one quaternary phosphorus atom may be a phosphonium group represented by the following general Formula (IV).



(IV)

In Formula (IV), each group R_1, R_2, R_3, and R_4 is independently selected from (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h), an alkoxy alkyl group, or (i) a polyether group.

The halide anion of the halide salt can be selected from an iodide ion (iodine ion) and a bromide ion (bromine ion).

Some exemplary halide salts are bromide salts or iodide salts of a tetraalkyl ammonium ion such as tetrabutyl ammonium, an imidazolium ion such as 1-ethyl-3-methyl imidazolium, a triazolium, a group comprising a tertiary sulfur atom, or a group

comprising a quaternary phosphorous atom. Among them, an imidazolium iodide such as 1-ethyl-3-methyl imidazolium iodide, a triazolium iodide, a tetraalkyl ammonium iodide such as tetrabutyl ammonium iodide and the like are often preferred as they exhibit an excellent performance as the photoelectric cell. One or more of such iodides may be used simultaneously.

In addition, the electrolyte of the present disclosure may contain halide metals such as LiI, NaI, and KI.

The total concentration of halide salts in the electrolyte solution may be 0.1 moles/liter or more, 0.2 moles/liter or more, or 0.4 moles/liter or more. The concentration of a halide salt may often preferably be 0.2 mole/liter or more, in order to attain photoelectric conversion efficiency almost equal to that of an electrolyte solution containing a halogen molecule such as I_2 and Br_2. The total concentration halide salts can be 10.0 moles/liter or less, 5 moles/liter or less, 2 moles/liter or less, or 1.8 moles/liter or less.

Conventionally, when used as an electrolyte solution for dye-sensitized solar cells, a halide salt has been combined with a halogen molecule to constitute an oxidation-reduction system, in which the coexistence of a halogen molecule was considered prerequisite. Thus, the electrolyte solution for dye-sensitized solar cells that uses a halide salt was inevitably colored.

However, the present inventors have found that a halide salt that is formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide ion group unexpectedly does not require the coexistence of a halogen molecule and can fully serve as an electrolyte without the coexistence of a halogen molecule. The electron-transporting performance is almost equal to when a halogen molecule is conventionally present. The battery performance such as the light conversion efficiency of a dye-sensitized solar cell is almost equal to that obtained using conventional electrolyte solutions that include a halogen molecule. When a halogen molecule is absent or present in a trace amount such as no greater than 0.0004 moles/liter, no color is produced and virtual colorlessness and transparency may be attained, thereby exhibiting various advantages as a dye-sensitized solar cell.

Though the mechanism of photoelectric conversion of a dye-sensitized solar cell has not been fully elucidated, it is known that when a dye (Dye) in a dye-sensitized solar cell absorbs light, it is excited to an active or excited state (Dye^*). When the excited dye (Dye^*) returns to the ground state, it supplies electrons to a semiconductor (for example titanium dioxide) and the excited state dye turns into a cation resulting in an electron-

deficient state (Dye^+). This mechanism can be represented by the following Reactions (1) and (2).

$$Dye \rightarrow Dye^* \qquad \text{Reaction (1)}$$

$$Dye^* \rightarrow Dye^+ + e^- \text{ (on } TiO_2) \qquad \text{Reaction (2)}$$

On the other hand, when a halide salt in the electrolyte solution is an iodide salt, it is believed, an iodide ion (I^-) ionized from the iodide salt reacts with an iodine molecule (I_2) coexistent in the electrolyte solution as in the following Reaction (3).

$$I_2 + I^- \rightarrow I_3^- \qquad \text{Reaction (3)}$$

This reaction results in the formation of I_3^- in the electrolyte solution. In the conventional electrolyte solution, iodine molecules have been added to form these anions. To these anions (I_3^-), electrons are supplied from a catalyst (Pt) present on the surface of the counter electrode, and the electrolyte solution donates electrons to and receives electrons from the counter electrode according to the following Reactions (4) and (5).

$$I_3^- + 2e^- \text{ (on Pt)} \rightarrow 3I^- \qquad \text{Reaction (4)}$$

$$3I^- + 3I_2 \rightarrow 3I_3^- \qquad \text{Reaction (5)}$$

The anions (I_3^-) that donated and received electrons in the electrolyte solution can supply electrons to the cationic dye (Dye^+) according to the following Reaction (6).

$$2Dye^+ + 2I_3^- \rightarrow 2Dye + 3I_3 \qquad \text{Reaction (6)}$$

The dye returns to the original state as a result of this reaction. Thus, the electrons generated at the dye-side electrode (i.e., photo anode) are passed through the battery load to the counter electrode, and further transmitted through the electrolyte solution constituting the oxidation-reduction system to complete the electrical circuit.

Conventionally, it was not always clear, but the reaction of a dye-sensitized solar cell using an electrolyte solution that constitutes an oxidation-reduction system comprising a halide salt similar to a halide salt defined by the present invention and a halogen molecule had been considered as described above. But according to one embodiment of the present invention, an electrolyte solution comprising a halide salt (for example, an imidazolium iodide such as 1-ethyl-3-methyl imidazolium iodide or a quaternary ammonium iodide such as triazolium iodide) defined by one embodiment of the present invention does not require the supply of halogen molecules and the battery reaction

proceeds normally without the coexistence of halogen molecules. The battery reaction is estimated to proceed according to, but not limited to, the following mechanism:

$Dye \rightarrow Dye^*$ Reaction (11)

$Dye^* \rightarrow Dye^+ + e^-$ (on TiO_2) Reaction (12)

$2Dye^+ + 2I^- \rightarrow 2Dye + I_2$ Reaction (13)

$I_2 + I^- \rightarrow I_3^-$ Reaction (14)

$I_3^- + 2e^- \rightarrow$ (on Pt) $\rightarrow 3I^-$ Reaction (15)

Since the above Reactions (13) and (14) may be summarized to the following equation (13'), the above Reactions (11)-(15) may be represented by the following series of reactions.

$Dye \rightarrow Dye^*$ Reaction (11)

$Dye^* \rightarrow Dye^+ + e^-$ (on TiO_2) Reaction (12)

$2Dye^+ + 3I^- \rightarrow 2Dye + I_3^-$ Reaction (13')

$I_3^- + 2e^- \rightarrow$ (on Pt) $\rightarrow 3I^-$ Reaction (15)

Thus, if the battery reaction is represented by the series of equations, it is thought that the supply (coexistence) of halogen molecules (iodine molecules) in the electrolyte solution is not necessary.

The above reaction sequence is thought to have been similar even for the conventional electrolyte solution in which halogen molecules were coexistent, and it was found in one embodiment of the present invention that the battery performance of the above battery reaction in which no halogen molecules were supplied was almost equal to that of the reaction in which the conventional halogen molecule were coexistent.

Thus, in one embodiment of the present invention, the electrolyte solution does not need to include any added halogen molecules. However, inclusion of halogen molecules does not necessarily deteriorate the battery performance, and thus the electrolyte solution according to one embodiment of the present invention may contain halogen molecules at a concentration range that does not stain the electrolyte solution. For example, the halogen molecule concentration can be 0.0004 moles/liter or less.

As used herein, the concentration (0.0004 moles/liter or less) of halogen molecules in the electrolyte solution of the present invention is the concentration of halogen molecules added as the component raw material of the electrolyte solution. It is the sum of halogen molecules added whether they occur as halogen molecules such as I_2 and Br_2 or as halide ions such as I_3^- and Br_3- in the electrolyte solution.

The concentration of halogen molecules such as I_2 and Br_2 in the electrolyte solution as used herein can be determined using a standard curve based on transmission

spectra created by using an electrolyte solution or a solvent of the same composition except for the amount of halogen molecules, and by varying the amount of halogen molecules. The rate of visible transmission may be calculated by taking into consideration a weighted coefficient at 380 nm to 780 nm in the visible range according to JIS A5759. In this case, the electrolyte solution separated from the battery may be determined.

Also, in an electrolyte solution for dye-sensitized solar cells according to one embodiment of the present invention, it is believed that even when halogen molecules are not supplied as the starting component, halogen molecules (halogen molecules such as I_2 and Br_2, and halide ions such as I_3^- and Br_3^-) are believed to be transiently present as shown in the above Reaction (13). However, the amount of such halogen molecules may be minute, negligible, or may be compared to the concentration of halide cation groups by the composition analysis of the electrolyte solution. Also, the amount of halogen molecules generated as the starting composition may be estimated by a quantitative analysis with transmission spectra. Thus, theoretically (if it could be analyzed), the amount of halogen molecules derived from the halides blended to the electrolyte solution should be excluded. Practically, however, the amount is minute and may be neglected (in this case, the amount of 0.0004 moles/liter or less including halogen molecules derived from the halides blended to the electrolyte solution is thought to correspond to the electrolyte solution of the present invention).

Other conventionally used electrolyte solutions that were not mentioned in the above but are known may be added unless they badly affect the present invention.

The electrolyte solution claimed in the present invention may be an organic solvent electrolyte solution. Suitable solvents that can be used include, but not limited to, conventionally known solvents. Suitable solvents preferably are electrochemically inactive, have a high specific dielectric constant, and have a low viscosity. Examples of such solvents include nitrile solvents such as methoxy propionitrile and methoxy acetonitrile, lactone solvents such as γ-butyrolactone and valerolactone, carbonate solvents such as ethylene carbonate and propylene carbonate, ethereal solvents such as dioxane, diethylether and ethylene glycol dialkylether, alcoholic solvents such as methanol, ethanol glycol monalkyleterh, polypropylene glycol monoalkylether, non-protic polar solvents such as dimethyl sulfoxide and sulfolane, glycolic solvents such as ethylene glycol and polyethylene glycol, methyl cellulose, ethyl cellulose, polyvinylidene fluoride, polymethyl methacrylate, polyacrylonitrile, and the like.

Among them, from the viewpoint of excellent characteristics mentioned above, nitrile solvents such as methoxy propionitrile, lactone solvents such as γ-butyrolactone, carbonate solvents such as propylene carbonate, and glycolic solvents such as

polyethylene glycol may preferably be used. More than one solvent may be used simultaneously.

Furthermore, the electrolyte solution according to one embodiment of the present invention may be an ionic liquid electrolyte solution (molten salt electrolyte solution). For example, ambient temperature-molten salts such as imidazolium salts and triazolium salts including 1-ethyl-3-methyl imidazolium tetrafluoroborate, 1-ethyl-3-methyl imidazolium bis(trifluoromethanesulfonyl)imide, and the like may be used.

The electrolyte solution claimed in the present invention may comprise a base in the electrolyte solution for offering characteristics such as electron transfer efficiency, photoelectric conversion efficiency, and enhanced durability. Some suitable bases comprise a ring structure having at least one nitrogen heteroatom. Such bases often contain a five or six membered ring having one or two nitrogen heteroatoms. Some bases have one or two nitrogen heteroatoms in a six-membered ring such as pyridine or pyrimidine. Examples include, but are not limited to, 4-tert-butyl pyridine (4-TBP), 2-picoline and 2,6-lutidine. Other bases have one or two nitrogen heteroatoms in a five membered ring such as imidazole. Examples include, but are not limited to, N-methyl benzimidazole. Other bases include a guanidium group such as guanidium thiocyanate and guanidium isothiocyanate, and the like. Among them, a base containing 4-tert-butyl pyridine, 2-picoline, 2,6-lutidine, N-methyl benzimidazole, a guanidium-containing group and a pyrimidine ring-containing group can favorably enhance electron transfer efficiency between the electrolyte and the counter electrode comprising a semiconductor electrode, photoelectric conversion efficiency and durability, and thus can be preferably used. More than one such additive may be used simultaneously. The concentration of the above base can be 0.1 moles/liter or more, 0.2 moles/liter or more or 0.4 moles/liter or more, and can be 10.0 moles/liter or less, 2.0 moles/liter or less or 1.8 moles/liter or less.

In the electrolyte solution for dye-sensitized solar cells according to one embodiment of the present invention, a halide salt alone formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide ion group can constitute an electrolyte solution. When a solvent is not used, the halide salt can be used as the electrolyte solution as it is. As needed or desired, a solvent or another constituent may be mixed as appropriate for production. The sequence of addition is not specifically limited.

A substrate for use in the dye-sensitized solar cell according to one embodiment of the present invention is not specifically limited, and a wide range of glass and/or plastic

substrates having a wide range of electric conductive layers commonly used in the dye-sensitized solar cell may be used.

As the glass and/or plastic substrate, a substance is often selected that is colorless and highly transparent, that is highly heat resistant, that has excellent chemical resistance and gas barrier properties, and that is low-cost. A plastic substrate that is flexible may be preferred. As the glass substrate, float glass such as soda-lime glass may be used. Suitable plastic substrates that can be used include polyethylene terephthalate (PET), polyethylene naphthalate (PEN), syndiotactic polystyrene (SPS), polyphenylene sulfide (PPS), polycarbonate (PC), polyacrylate (PAr), polysulfone (PSF), polyestersulfone (PES), polyetherimide (PEI), transparent polyimide (PI) and the like. Among them, in terms of chemical resistance and cost, polyethylene terephthalate (PET) and polyethylene naphthalate (PEN) are preferred.

The electrode for use in the substrate is not specifically limited, and a wide variety of electrodes commonly used in dye-sensitized solar cells including metals such as platinum, gold, silver, copper, aluminum and indium, carbon such as graphite, carbon black, glassy carbon, carbon nanotube and fullerene, or conductive metal oxides such as an indium-tin composite oxide, a tin oxide and an antimony-doped tin oxide can be used. Among them, in terms of optical transparency, conductive metal oxides are often preferred with an indium-tin composite oxide (ITO) and a zinc oxide being specifically preferred. The thickness of the electrode can be 0.01 micrometers (μm) to 5 micrometers, which corresponds to the thickness commonly used in dye-sensitized solar cells.

The material, thickness, porous factors, and the like of a porous metal oxide semiconductor are not specifically limited, and a wide variety of substances commonly used in dye-sensitized solar cells include metals such as titanium oxides such as titanium dioxide and anatase-type titanium dioxide, zinc oxide, tin oxide, and the like. Specifically the thickness of the semiconductor layer can be 0.1 to 50 μm.

The type of a dye molecule to be used for sensitization is not specifically limited and there can be used a wide variety of dyes commonly used in dye-sensitized solar cells including cyanine-, merocyanine-, oxonol-, xanthene-, squarylium-, polymethine-, coumarin-, riboflavin- and perylene-series organic dyes, complex dyes such as Ru complexes and metal phthalocyanine derivatives, metal porphyrin derivatives and chlorophyll derivatives, and synthetic and natural dyes described in "KINO ZAIRYO (Functional Materials)", 2003 June, pages 5-18, and organic dyes centering on coumarins described in J. Chem. Phys., B. Vol. 107, page 597 (2003), and the concentrations used may be 4×10^{-3} moles/liter or more, for example.

For items that are related to the dye-sensitized solar cells but not described in the above such as a polymer electrode and the viscosity of the electrolyte solution, those commonly and preferably used in the dye-sensitized solar cells may be used unless they badly affect the components contained in the electrolyte solution claimed in the present invention.

Furthermore, from the viewpoint of offering a design, batteries may be colored.

EXAMPLES

Method of measuring I_2 concentration

The concentration of halogen molecules such as I_2 and Br_2 in the electrolyte solution may be calculated by measuring the transmission spectrum.

Specifically, the transmission spectrum of an iodine solution in the subject solvent can be measured to create a standard curve on the rate of visible transmission and the iodine concentration. The transmission spectrum of an electrolyte solution can be measured and then converted from the standard curve. The rate of visible transmission may be calculated by taking into consideration a weighted coefficient at 380 nm to 780 nm in the visible range according to JIS A5759.

Herein below, the film, ink, dye, counter electrode, sealing agent, electrode components, solvent etc. used in one embodiment of the present invention are described in detail.

Transparent electric conductive film (manufacturer: Teijin DuPont Films Japan Limited, part number: Q65FA, on which ITO was sputtered to a transmission of 80% and a surface resistance of 15 ohm/□; transmission, 80% measured in the range of 380 to 780 nm);

TiO_2 ink (manufacturer: Peccell Technologies, Inc., part number: PECC-01-06);

N719 dye (manufacturer: Peccell Technologies, Inc., part number: PEDC07; specifically, N719 as used herein represents cis-bis(isothiocyanate)bis(2,2'-bipyridyl-4,4'-dicarboxylate)-ruthenium(II)bis-tetrabutyl ammonium);

Dye absorbing solution (the above N719 was dissolved in acetonitrile: t-butyl alcohol: ethanol = 2:1:1);

Counter electrode (manufacturer: Peccell Technologies, Inc., part number: PECF-CAT);

Transmission counter electrode (manufacturer: Peccell Technologies, Inc., trade designation: See-Through counter electrode);

Sealing agent (manufacturer: DuPont, trade name: Surlyn™, thickness: 50 μm);

1-ethyl-3-methylimidazolium iodide (manufacturer: Tokyo Chemical Industry Co., Ltd., part number: E0556);

Tetrabutyl ammonium iodide (manufacturer: Tokyo Chemical Industry Co., Ltd., part number: T0057);

4-tert-butyl pyridine (manufacturer: Tokyo Chemical Industry Co., Ltd., part number: B0388);

Guanidium isothiocyanate (manufacturer: Tokyo Chemical Industry Co., Ltd., part number: G0230);

γ-butyrolactone (manufacturer: Wako Pure Chemical Industries, Ltd., part number: 022-07985);

Propylene carbonate (manufacturer: Tokyo Chemical Industry Co., Ltd., part number: P0525); and

Epoxy adhesive (manufacturer: Sumitomo 3M Limited, part number: DP100 Clear).

Working Example 1

Preparation of an electrolyte solution

0.47614 grams of 1-ethyl-3-methylimidazolium iodide, 0.73874 grams of tetrabutyl ammonium iodide, 0.13521 grams of 4-tert-butyl pyridine and 0.5908 grams of guanidium isothiocyanate were dissolved in 5 mL (milliliters) of propylene carbonate at ambient temperature and ambient humidity to prepare an electrolyte solution, which was used in the following Working Example 2. Furthermore, the type and/or concentration of each component was changed, and the resultant solution was used in other examples.

Working Examples 2 to 7

Production of a dye-sensitized solar cell

Using the above materials, a dye-sensitized solar cell of the present example was produced using the concentration of each component in the electrolyte solution shown in Table 1 according to Step 1 to 5 shown in Fig. 1.

To a ITO-PEN film (1), TiO_2 ink was applied for form a TiO_2 film (2) using a doctor blade (manufacturer: Peccell Technologies, Inc., part number: PECE-DB) method to an area of 10 mm × 10 mm and a wet film thickness of 70 μm, and then dried in a 150°C high temperature drying oven for 30 minutes (Step 1). Then the resulting film was immersed in 0.0003 moles/liter dye-adsorbing solution at 40°C for 2 hours so as to allow

the above dye to be adsorbed (3) on the surface of TiO_2, and then removed from the adsorbing solution and washed once in acetonitrile (Step 2). The above film (1) and the counter electrode (5) were adhered with an epoxy adhesive so as to sandwich the sealing agent (4) (Step 3). Through a hole (6) on the counter electrode, the electrolyte solution (7) concerning the present invention was injected (Step 4). The hole of the counter electrode was sealed with an epoxy resin (8) (Step 5).

Summary of numbers in Figure 1: (1) ITO-PEN film; (2) TiO_2 film; (3) dye on surface of TiO_2; (4) sealing agent; (5) Pt/Ti-PEN transmission-type counter electrode; (6) injection port for electrolyte solution; (7) electrolyte solution; and (8) epoxy resin.

Working Example 8

Production of a transmission dye-sensitized solar cell

The transmission dye-sensitized solar cell of Working Example 8 was produced using the concentration of each component in the electrolyte solution shown in Table 2 in a manner similar to that in Working Example 7 except that in the above Step 3, the counter electrode was replaced with a transmission counter electrode. Two kinds of samples having an active area of 0.28 cm^2 and 41.28 cm^2 were prepared.

Comparative Example 1

Production of a I_2-containing transmission dye-sensitized solar cell

A transmission dye-sensitized solar cell was produced in a manner similar to that in Working Example 7 except that the concentration of 1-ethyl-3-methylimidazolium iodide was 0.4 moles/liter and that of I_2 was 0.04 moles/liter (the concentration of each component in the electrolyte solution is described in Tables 1 and 2).

Measurement of conversion efficiency, etc.

For the films of Working Examples 2 to 8 and Comparative Example 1, the conversion efficiency, open voltage value (V_{OC}), short-circuit current value (I_{SC}), short-circuit current density (J_{SC}), fill factor (FF), maximum output point (P_{max}), maximum voltage (V_{max}) and maximum current (I_{max}) were measured using the measurement instruments described below.

Instruments used: Solar simulator and IV Curve Analyzer (manufacturer: Peccell Technologies, Inc., part number: PEC-L11, PECK2400-N)

Software used for measurement: Peccell I-V curve analyzer (manufacturer: Peccell Technologies, Inc.)

The results are shown in Tables 1 and 2. The designation A and B in Table 2 indicate the direction of the irradiated light. The designation A refers to the direction of the irradiated light being on the TiO2 side and the designation B refers to the direction of irradiated light being on the electrolyte side.

As can be seen from Tables 1 and 2, the electrolyte solution of Working Examples 2 to 8 exhibit characteristics almost similar to that of conventional Comparative Example 1 containing I_2.

Table 1:

Electrolyte solution No.	Electrolyte solution						Active area (cm^2)	Light intensity at the time of measuring characteristics	Efficiency (%)	Open voltage (V)	Short-circuit current density (mA/cm2)	Fill factor
	I2 (moles/liter)	1-ethyl-3-methyl imidazolium iodide (moles/liter)	tert-butyl ammonium iodide (moles/liter)	4-tertbutyl pyridine (moles/liter)	Guanidium isothiocyanate (moles/liter)	Solvent						
Work. Ex. 2	0	0.4	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	3.05	0.75	6.94	0.58
Work. Ex. 3	0	0.8	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	3.18	0.77	6.46	0.63
Work. Ex. 4	0	1.2	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	3.13	0.74	7.00	0.59
Work. Ex. 5	0	0.4	0.4	0.2	0.1	γ-butyro lactone	0.28	1SUN AM1.5	2.67	0.72	5.37	0.69
Work. Ex. 6	0	0.4	0.4	0.2	0.1	Methoxy propionitrile	0.28	1SUN AM1.5	3.11	0.79	6.14	0.64
Work. Ex. 7	0	0.8	0.4	0.2	0.1	γ-butyro lactone	0.28	1SUN AM1.5	2.76	0.74	6.74	0.55
Comp. Ex. 1	0.04	0.4	0.4	0.2	0.1	Methoxy propionitrile	0.28	1SUN AM1.5	2.98	0.76	6.27	0.62

Table 2:

Electrolyte solution No.	Electrolyte solution					Active area (cm2)	Light intensity at the time of measuring characteristics	Light incidence plane at the time of measuring characteristics	Efficiency (%)	Open voltage (V)	Short-circuit current density (mA/cm2)	Fi fac
	I2 (moles/liter)	1-ethyl-3-methyl imidazolium iodide (moles/liter)	tert-butyl ammonium iodide (moles/liter)	4-tertbutyl pyridine (moles/liter)	Guanidium isothiocyanate (moles/liter)	Solvent						
Work. Ex. 2	0	0.4	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	A	1.59	0.72	3.68	0.5
Work. Ex. 2	0	0.4	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	B	1.12	0.70	2.38	0.6
Comp. Ex. 1	0.04	0.4	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	A	1.22	0.66	2.78	0.6
Comp. Ex. 1	0.04	0.4	0.4	0.2	0.1	Propylene carbonate	0.28	1SUN AM1.5	B	0.51	0.65	1.28	0.6

Electrolyte solution No.	Electrolyte solution					Active area (cm2)	Light intensity at the time of measuring characteristics	Light incidence plane at the time of measuring characteristics	Maximum electric power Pmax (mW)	Voltage at maximum output (V)	Current at maximum output (mA)	-
	I2 (moles/liter)	1-ethyl-3-methyl imidazolium iodide (moles/liter)	tert-butyl ammonium iodide (moles/liter)	4-tertbutyl pyridine (moles/liter)	Guanidium isothiocyanate (moles/liter)	Solvent						
Work. Ex. 8	0	0.8	0.4	0.2	0.1	γ-butyro lactone	41.28	800 lux	A	0.48	0.48	1.0	-
Work. Ex. 8	0	0.8	0.4	0.2	0.1	γ-butyro lactone	41.28	800 lux	B	0.31	0.49	0.63	-
Comp. Ex. 2	0.04	0.4	0.4	0.2	0.1	Propylene carbonate	41.28	800 lux	A	0.067	0.41	0.16	-
Comp. Ex. 2	0.04	0.4	0.4	0.2	0.1	Propylene carbonate	41.28	800 lux	B	0.07	0.35	0.022	-

Measurement of deteriorated characteristics

For the characteristics of the dye-sensitized solar cell produced in Working Example 2 and Comparative Example 1, the degree of its deterioration by irradiation of pseudo-sunlight of AM1.5, 1SUN was determined with time using the short-circuit current value at ambient temperature and ambient humidity.

Instruments used: Solar simulator and IV Curve Analyzer (manufacturer: Peccell Technologies, Inc., part number: PEC-L11, PECK2400-N).

Software used for measurement: Peccell I-V curve analyzer (manufacturer: Peccell Technologies, Inc.).

Samples measured: On an area of 10 mm × 10 mm of the dye-sensitized solar cell, a measurement area was made constant using a mask with an opening of 6 mm in diameter. The result is shown in Table 3. The degree of changes in characteristics with the initial value set as 100% when 1SUN, AM1.5 was continuously irradiated

Table 3:

Hours later	Work. Ex. 2	Comp. Ex. 1
0	100	100
100	109	127
200	106	122
300	102	118
400	100	115

As can be seen from Table 3, the sample of Working Example 2 was stable for 400 hours.

Working Examples 9 to 12 and Comparative Example 2

Measurement of effect of I_2 concentration on the light transmission spectrum in the visible region

To the electrolyte solution of Working Example 7, I_2 was added at a concentration of 0.000004 moles/liter (Working Example 9), 0.00004 moles/liter (Working Example 10), 0.0004 moles/liter (Working Example 11), 0.004 moles/liter (Working Example 12), and 0.04 moles/liter (Comparative Example 2). The transmission spectrum in the visible region was determined using the following measuring instrument at ambient temperature and ambient humidity.

Cell used: A standard quartz cell of 10 mm square.

UV-VIS spectrum meter: Hitachi, Ltd., part number: U-3310.

In the measurement of the rate of visible transmission, a weighted coefficient at 380 nm to 780 nm in the visible range according to JIS A5759 was taken into consideration.

As can be seen from Table 4 and Fig. 2, the sample is visually recognized to be transparent only when the I_2 concentration is 0.0004 (moles/liter) or less.

Table 4: Relationship between the iodine concentration and the rate of transmission

Iodine concentration (moles/liter)	Rate of transmission (%)	Rate of transmission at each wavelength (%)	
0	98.8	300 nm: 0 600 nm: 99.4	400 nm: 88.1 700 nm: 99.6	500nm: 98.1 800nm: 99.6
0.000004	98.8	300 nm: 0 600 nm: 99.4	400 nm: 77 700nm: 99.6	500nm: 97.9 800nm: 99.6
0.00004	97.5	300 nm: 0 600 nm: 99.2	400 nm: 29.5 700 nm: 99.8	500nm: 95.5 800nm: 99.7
0.0004	88	300 nm: 0 600 nm: 95.8	400 nm: 0 700 nm: 99.5	500nm: 76.9 800nm: 99.6
0.004	41.2	300 nm: 0 600 nm: 67	400 nm: 0 700 nm: 98.5	500nm: 8.4 800nm: 99.6
0.04	2.6	300 nm: 0 600 nm: 2	400 nm: 0 700 nm: 88	500nm: 0 800nm: 99.1

* Iodine concentration is only shown.

Working Examples 13 to 17

Measurement of effect of an iodide on photoelectric conversion efficiency

Light intensity conversion efficiency was determined at ambient temperature and ambient humidity in a manner similar to Working Example 7 except that instead of the combination of 1-ethyl-3-methylimidazolium iodide, tetrabutyl ammonium iodide, 4-tert-butyl pyridine and guanidium isothiocyanate, the halide salt 1-ethyl-3-methylimidazolium iodide alone was used at a concentration of 0.1 moles/liter (Working Example 17), 0.2 moles/liter (Working Example 13), 0.4 moles/liter (Working Example 14), 0.8 moles/liter (Working Example 15) and 1.2 moles/liter (Working Example 16). The solvent used was propylene carbonate. .

Table 5:

No.	Working Ex. 17	Working Ex. 13	Working Ex. 14	Working Ex. 15	Working Ex. 16
1-ethyl-3-methylimidazolium iodide	0.1 moles/liter	0.2 moles/liter	0.4 moles/liter	0.8 moles/liter	1.2 moles/liter
Efficiency/%	0.89	1.52	1.78	1.72	1.57

As can be seen from Table 5, when the iodide concentration is 0.2 moles/liter or more, the photoelectric conversion efficiency is 1.5% or more, which is almost equal to the value of the conventional dye-sensitized solar cell containing I_2 as the oxidation-reduction pair (Table 2, Comparative Example 1).

Results

The foregoing confirmed that in accordance with the present invention there can be provided an excellent electrolyte solution for dye-sensitized solar cells that has good light transmission at 400-700 nm, that has photoelectric conversion efficiency almost equal to that of the conventional I_2-containing electrolyte solution and that has no deterioration in performance characteristics.

WE CLAIM:

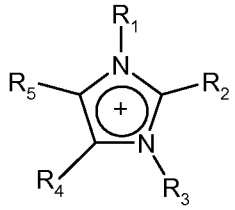
1. An electrolyte solution for dye-sensitized solar cells, said electrolyte solution comprising a halide salt formed of a cation comprising one or more groups containing at least one of quaternary nitrogen atom, tertiary sulfur atom or quaternary phosphorus atom, and an anion comprising a halide ion group, wherein the electrolyte solutions contains halogen molecules in a range of 0 to 0.0004 moles/liter.

2. The electrolyte solution for dye-sensitized solar cells according to claim 1, said electrolyte solution further comprising a solvent or an ionic liquid.

3. The electrolyte solution for dye-sensitized solar cells according to claim 2, wherein the concentration of said halide salt is 0.2 moles/liter or more.

4. The electrolyte solution for dye-sensitized solar cells according to claim 1, wherein said halide ion is an iodide ion and said halogen molecules are iodine molecules.

5. The electrolyte solution for dye-sensitized solar cells according to any one of claims 1 to 4, wherein said cation group comprising one or more groups containing at least one quaternary nitrogen atom is an imidazlium-type group of Formula (Ia)



(Ia)

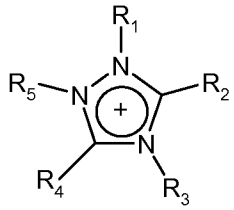
wherein

each group R_1 and R_3 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, or (i) a polyether group; and

each group R_2, R_4 and R_5 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an

alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, (i) a polyether group, or (j) hydrogen.

6. The electrolyte solution for dye-sensitized solar cells according to any one of claims 1 to 4, wherein said cation group comprising one or more groups containing at least one quaternary nitrogen atom is an triazolium-type group of Formula (Ia)



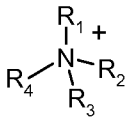
(Ib)

wherein

each group R_1, R_3, and R_5 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, or (i) a polyether group; and

each group R_2 and R_4 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, (i) a polyether group, or (j) hydrogen.

7. The electrolyte solution for dye-sensitized solar cells according to any one of claims 1 to 4, wherein said cation group comprising one or more groups containing at least one quaternary nitrogen atom is an ammonium group of Formula (II)



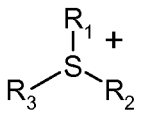
(II)

wherein

each group R_1, R_2, R_3, and R_4 is independently (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an

alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h) an alkoxy alkyl group, or (i) a polyether group.

8. The electrolyte solution for dye-sensitized solar cells according to any one of claims 1 to 4, wherein said cation group comprising one or more groups containing at least one tertiary sulfur atom is a sulfonium group of Formula (III)

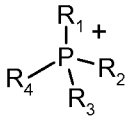


(III)

wherein

each group R_1, R_2, and R_3 is independently selected from (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h), an alkoxy alkyl group, or (i) a polyether group.

9. The electrolyte solution for dye-sensitized solar cells according to any one of claims 1 to 4, wherein said cation group comprising one or more groups containing at least one quaternary phosphorus atom is a phosphonium group of Formula (IV)



(IV)

wherein

each group R_1, R_2, R_3 and R_4 is independently selected from (a) a linear or branched alkyl group having 1-20 carbon atoms, (b) a linear or branched alkoxy group having 1-20 carbon atoms, (c) a fluorinated alkyl group having 1-20 carbon atoms, (d) an alkenyl group, (e) an alkynyl group, (f) any combination of groups (a) to (e), (g) any group (a) to (f) substituted with a halogen atom, (h), an alkoxy alkyl group, or (i) a polyether group.

10. The electrolyte solution for dye-sensitized solar cells according to any one of claims 1 to 9, said electrolyte solution further comprising at least one base having a

group having one nitrogen in a five-membered ring or a six-membered ring, two nitrogens in a five-membered ring or six-membered ring, or a guanidium group.

11. The electrolyte solution for dye-sensitized solar cells according to claim 10, said base comprising 4-tert-butyl pyridine, 2-picoline, 2, 6-lutidine, pyrimidine, N-methyl benzimidazole, guanidium thiocyanate, guanidium isothiocyanate, or a combination thereof.

12. The electrolyte solution for dye-sensitized cells according to any one of claims 10 or 11, wherein the base is present in an amount equal to at least 0.2 moles/liter.

13. A dye-sensitized solar cell comprising an electrolyte solution according to claim 1.

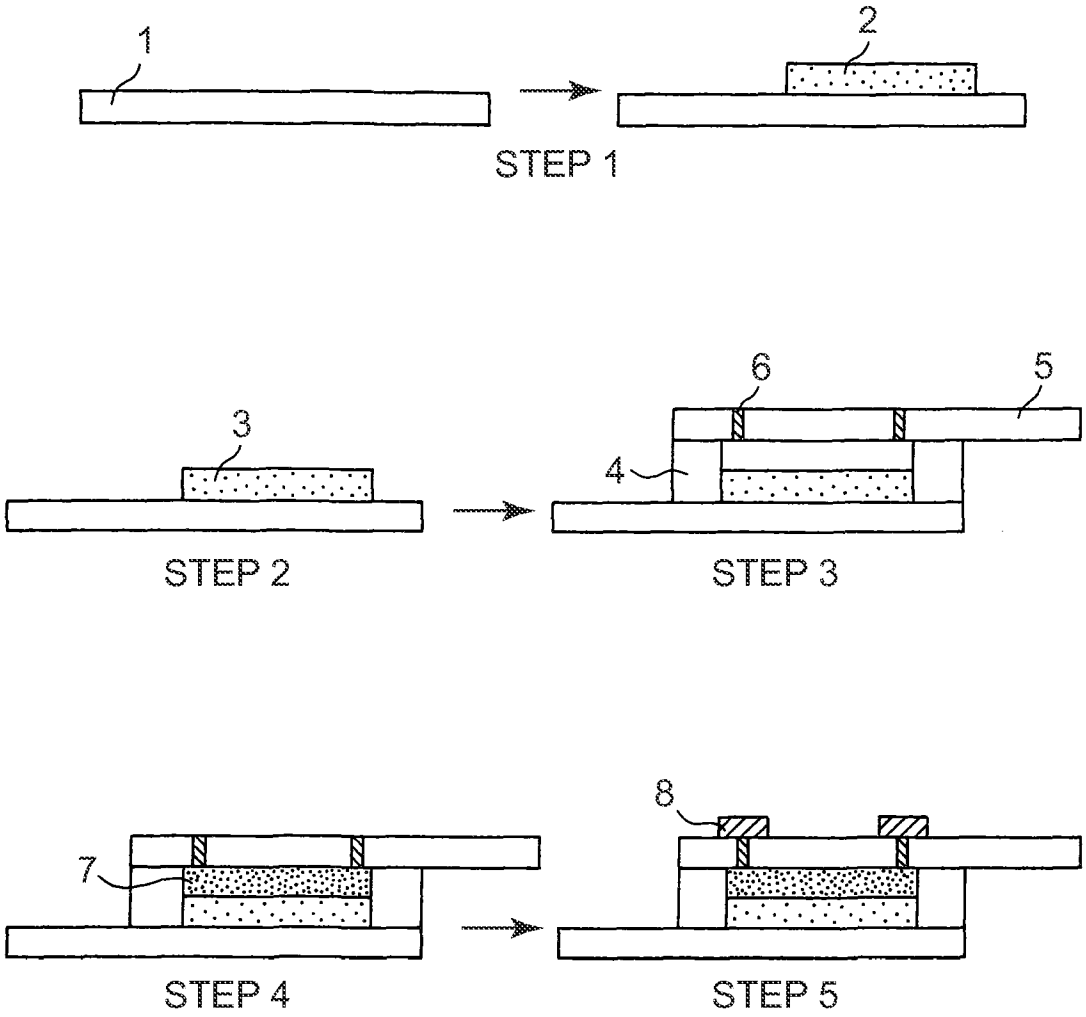


Fig. 1

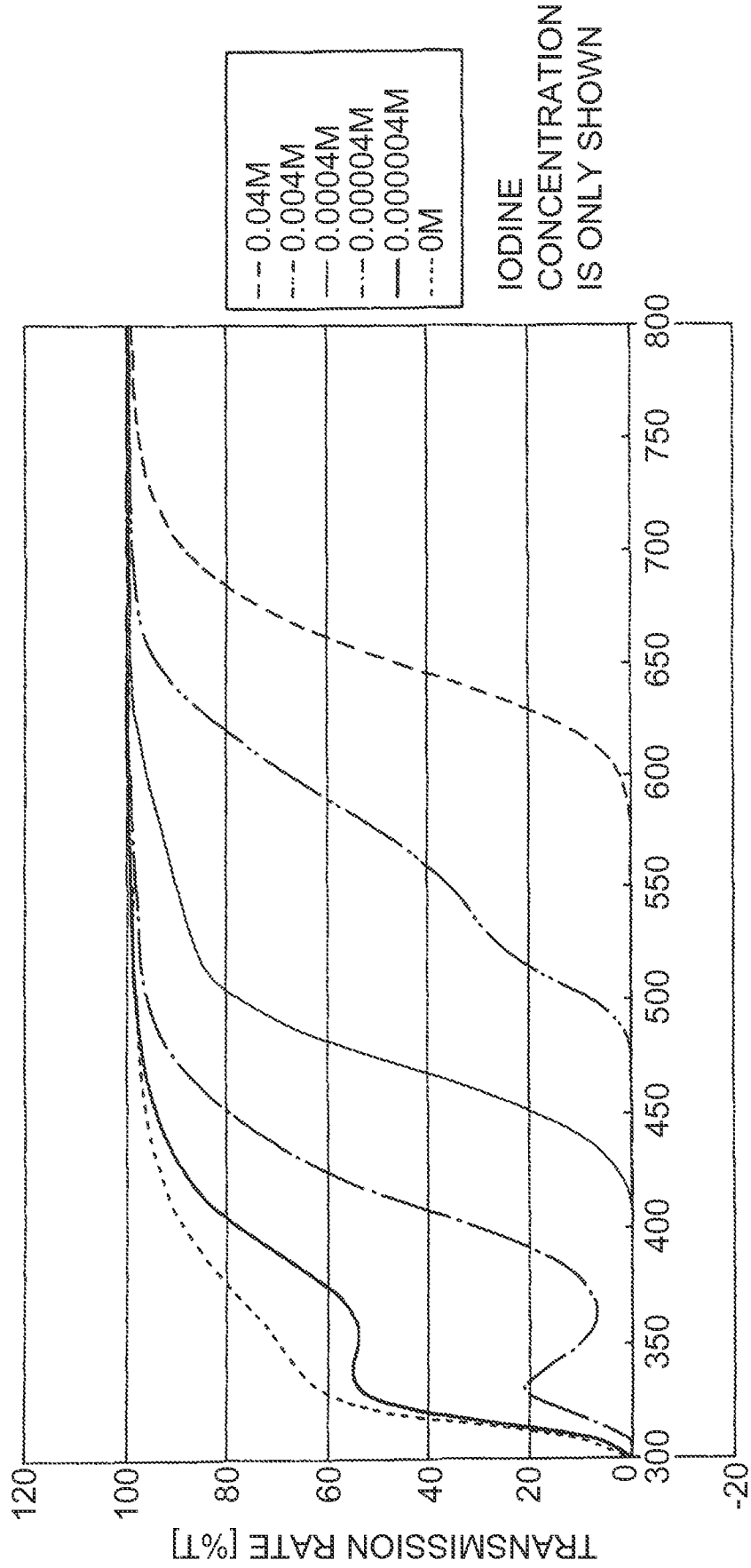

0.04M
0.004M
0.00004M
0.000004M
0.0000004M
0M
IODINE CONCENTRATION IS ONLY SHOWN
TRANSMISSION RATE [%T]
120
100
80
60
40
20
0
-20
300
350
400
450
500
550
600
650
700
750
800
WAVELENGTH [nm]

Fig. 2