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(54) **METHOD FOR PRODUCING CARBON MATERIAL**

(57) The present invention provides a method for manufacturing diamond, comprising electrolytically reducing carbon dioxide into diamond to obtain diamond in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein the electrolytic solution comprises an ionic liquid.

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Description

Technical Field

[0001] The present disclosure relates to a method for manufacturing a carbon material, and more specifically to a method for manufacturing a carbon material by electrolytically reducing carbon dioxide.

Background Art

[0002] The development of a technique related to carbon recycle which regards carbon dioxide as a carbon resource and involves recovering and recycling it as diverse carbon compounds has been demanded as a measure against recent global warming.

[0003] As for such a technique, a method involving decomposing carbon dioxide to fix carbon in the carbon dioxide, for example, a method for depositing diamond on a cathode by electrolysis of carbon dioxide using a high-temperature molten salt (see Patent Literature 1) has been proposed.

[0004] Electrolysis of carbon dioxide using a mixture of two ionic liquids of N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) and 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), a Ni electrode as a cathode, and a Pt electrode as an anode suggests production of a carbon material on the cathode (see Non Patent Literature 1).

Citation List

Patent Literature

[0005] Patent Literature 1: JP-2016-89230 A

Non Patent Literature

[0006] Non Patent Literature 1: 49th International conference on Environmental Systems ICES-2019-141, 2019, Boston

Summary of Invention

Technical Problem

[0007] In the former method, since a high-temperature molten salt is used, energy is required for heating, and expensive equipment with heat resistance is required, and hence, there is a cost problem. Besides, work at high temperatures is required, and hence, there is also a safety problem. On the other hand, in the latter method, studies are made by variously changing a mixing ratio of the two ionic liquids of DEME-TFSI and BMIM-BF₄ and an electrolysis potential, then electrolysis is carried out at -1.0 V (against a silver pseudo reference electrode) at a mixing ratio between DEME-TFSI and BMIM-BF₄ of

25:75 (% by mol), and the cathode product is subjected to SEM/EDS analysis, thereby suggesting production of carbon, but details including whether carbon has been actually deposited or not are unknown because a Raman spectrum or the like has not been acquired, and besides, there is a problem that the accurate electrolysis potential is unknown because a pseudo reference electrode is used.

[0008] An object of the present disclosure is to provide a method for manufacturing a carbon material by conveniently reducing carbon dioxide at low energy.

Solution to Problem

[0009] The present disclosure includes the following embodiments.

[1] A method for manufacturing a carbon material, comprising electrolytically reducing carbon dioxide to obtain a carbon material in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein the electrolytic solution comprises an ionic liquid.

[2] The method for manufacturing a carbon material according to [1], wherein the anode is a Pt electrode, and the cathode is a Ag electrode.

[3] The method for manufacturing a carbon material according to [1] or [2], wherein the ionic liquid is an imidazolium-based ionic liquid, an aromatic ionic liquid, a pyrrolidinium-based ionic liquid, an ammonium-based ionic liquid, a piperidinium-based ionic liquid, or a quaternary phosphonium-based ionic liquid.

[4] The method for manufacturing a carbon material according to [1] or [2], wherein the ionic liquid is N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate (DEME-BF₄), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP₁₃-TFSI), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-TFSI), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), triethylpentylphosphonium bis (trifluoromethanesulfonyl) imide (P₂₂₂₅-TFSI), triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide (P₂₂₂₈-TFSI), or tributylmethylphosphonium bis (trifluoromethanesulfonyl) imide (P₄₄₄₁-TFSI).

[5] The method for manufacturing a carbon material according to any one of [1] to [4], wherein the electrolytic solution comprises a supporting electrolyte.

[6] An electrolytic reduction method comprising electrolytically reducing carbon dioxide in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein carbon dioxide is selectively electrolytically reduced into a carbon material selected from the group consisting of diamond, graphite, glassy

carbon, amorphous carbon, carbon nanotube, carbon nanohorn, and graphene by a potential to be applied to between the anode and the cathode.

[7] The electrolytic reduction method according to [6], wherein the electrolytic solution comprises an ionic liquid.

[8] An electrolytic reduction method comprising electrolytically reducing carbon dioxide in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein the electrolytic solution comprises an ionic liquid.

[9] The electrolytic reduction method according to any one of [6] to [8], wherein the anode is a Pt electrode, and the cathode is a Ag electrode.

[10] The electrolytic reduction method according to any one of [7] to [9], wherein the ionic liquid is an imidazolium-based ionic liquid, an aromatic ionic liquid, a pyrrolidinium-based ionic liquid, an ammonium-based ionic liquid, a piperidinium-based ionic liquid, or a quaternary phosphonium-based ionic liquid.

[11] The electrolytic reduction method according to any one of [7] to [9], wherein the ionic liquid is N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate (DEME-BF₄), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP₁₃-TFSI), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-TFSI), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄), triethylpentylphosphonium bis (trifluoromethanesulfonyl) imide (P₂₂₂₅-TFSI), triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide (P₂₂₂₈-TFSI), or tributylmethylphosphonium bis (trifluoromethanesulfonyl) imide (P₄₄₄₁-TFSI).

[12] The electrolytic reduction method according to any one of [6] to [11], wherein the electrolytic solution comprises a supporting electrolyte.

[13] The electrolytic reduction method according to [12], wherein the supporting electrolyte is KHCO₃, KHPO₄, LiBF₄, LiPF₆, LiClO₄, LiAsF₆, LiTf, LiTFSI, LiFSI, K₂CO₃, Li₂CO₃, Na₂CO₃, or NaHCO₃.

[14] The electrolytic reduction method according to [12] to [13], wherein the supporting electrolyte is LiBF₄, LiPF₆, LiTFSI, or LiFSI.

[15] The electrolytic reduction method according to any one of [12] to [14], wherein a concentration of the supporting electrolyte contained in the ionic liquid is from 0.01 mol/L to a saturated concentration.

[16] The electrolytic reduction method according to any one of [6] to [15], wherein the electrolytic reduction apparatus further comprises a reference electrode, the reference electrode is a Ag⁺/Ag electrode, and a potential of the cathode is -5.0 V to -0.5 V.

[17] The electrolytic reduction method according to any one of [6] to [16], wherein a temperature of the electrolytic solution is 0 to 100°C.

[18] The electrolytic reduction method according to any one of [6] to [17], wherein the carbon dioxide is reduced into diamond.

[19] An electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein the electrolytic solution comprises an ionic liquid.

[20] The electrolytic reduction apparatus according to [19], wherein the anode is a Pt electrode, and the cathode is a Ag electrode.

[21] The electrolytic reduction apparatus according to [19] to [20], wherein the ionic liquid is an imidazolium-based ionic liquid, an aromatic ionic liquid, a pyrrolidinium-based ionic liquid, an ammonium-based ionic liquid, a piperidinium-based ionic liquid, or a quaternary phosphonium-based ionic liquid.

[22] The electrolytic reduction apparatus according to any one of [19] to [21], wherein the ionic liquid is N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate (DEME-BF₄), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), triethylpentylphosphonium bis (trifluoromethanesulfonyl) imide (P₂₂₂₅-TFSI), triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide (P₂₂₂₈-TFSI), or tributylmethylphosphonium bis (trifluoromethanesulfonyl) imide (P₄₄₄₁-TFSI).

[23] The electrolytic reduction apparatus according to any one of [19] to [21], wherein the electrolytic solution comprises a supporting electrolyte.

[24] The electrolytic reduction apparatus according to [23], wherein the supporting electrolyte is KHCO₃, KHPO₄, LiBF₄, LiPF₆, LiClO₄, LiAsF₆, LiTf, LiTFSI, LiFSI, K₂CO₃, Li₂CO₃, Na₂CO₃, or NaHCO₃.

[25] The electrolytic reduction apparatus according to [23] to [24], wherein the supporting electrolyte is LiBF₄, LiPF₆, LiTFSI, or LiFSI.

[26] The electrolytic reduction apparatus according to any one of [18] to [20], wherein a concentration of the supporting electrolyte contained in the ionic liquid is from 0.01 mol/L to a saturated concentration.

[27] The electrolytic reduction apparatus according to any one of [19] to [26], wherein the carbon dioxide is reduced into diamond.

Advantageous Effects of Invention

[0010] According to the present disclosure, a carbon material can be manufactured by efficiently reducing carbon dioxide at a low cost.

Brief Description of Drawings

[0011]

[Figure 1] Figure 1 is a diagram schematically showing an experiment apparatus used in an experiment.
[Figure 2] Figure 2 is a cyclic voltammogram illus-

trating the reduction behavior of carbon dioxide during electrolytic reduction carried out using electrolytic solution A.

[Figure 3] Figure 3 is a graph showing time change of current during constant potential electrolytic reduction carried out using electrolytic solution A.

[Figure 4] Figure 4 is a graph showing measurement results of Raman spectra of a Ag electrode surface after constant potential electrolytic reduction carried out using electrolytic solution A.

[Figure 5] Figure 5 is a cyclic voltammogram illustrating the reduction behavior of carbon dioxide during electrolytic reduction carried out using electrolytic solution B.

[Figure 6] Figure 6 is a graph showing time change of current during constant potential electrolytic reduction at -2.60 V carried out using electrolytic solution B.

[Figure 7] Figure 7 is a graph showing time change of current during constant potential electrolytic reduction at -3.00 V carried out using electrolytic solution B.

[Figure 8] Figure 8 is a graph showing time change of current during constant potential electrolytic reduction at -3.15 V carried out using electrolytic solution B.

[Figure 9] Figure 9 is a graph showing time change of current during constant potential electrolytic reduction at -3.25 V carried out using electrolytic solution B.

[Figure 10] Figure 10 is a graph showing time change of current during constant potential electrolytic reduction at -3.70 V carried out using electrolytic solution B.

[Figure 11] Figure 11 is a graph showing measurement results of Raman spectrum of a Ag electrode surface after constant potential electrolytic reduction at -2.60 V carried out using electrolytic solution B.

[Figure 12] Figure 12 is a graph showing measurement results of Raman spectrum of a Ag electrode surface after constant potential electrolytic reduction at -3.00 V carried out using electrolytic solution B.

[Figure 13] Figure 13 is a graph showing measurement results of Raman spectrum of a Ag electrode surface after constant potential electrolytic reduction at -3.15 V carried out using electrolytic solution B.

[Figure 14] Figure 14 is a graph showing measurement results of Raman spectrum of a Ag electrode surface after constant potential electrolytic reduction at -3.25 V carried out using electrolytic solution B.

[Figure 15] Figure 15 is a graph showing measurement results of Raman spectrum of a Ag electrode surface after constant potential electrolytic reduction at -3.70 V carried out using electrolytic solution B.

[Figure 16] Figure 16 is a cyclic voltammogram illustrating the reduction behavior of carbon dioxide during electrolytic reduction in Example 12 and Comparative Example 3.

[Figure 17] Figure 17 is a cyclic voltammogram illustrating the reduction behavior of carbon dioxide during electrolytic reduction in Example 13 and Comparative Example 4.

[Figure 18] Figure 18 is a cyclic voltammogram illustrating the reduction behavior of carbon dioxide during electrolytic reduction in Example 14 and Comparative Example 5.

10 Description of Embodiments

[0012] Hereinafter, the present disclosure will be described in detail.

[0013] The present disclosure provides a method for manufacturing a carbon material, comprising electrolytically reducing carbon dioxide to obtain a carbon material in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, and this electrolytic reduction apparatus.

[0014] The method for manufacturing a carbon material according to the present disclosure utilizes electrolytic reduction.

[0015] Thus, the present disclosure also provides a method for electrolytically reducing carbon dioxide in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide.

[0016] The electrolytic reduction is usually performed in an electrolyzer. For example, the electrolyzer may be of single-chamber type, double-chamber type, PEM type (solid polymer membrane type), flow type, or a bipolar type.

[0017] The electrolytic reduction apparatus for use in the electrolytic reduction method has an anode, a cathode, and an electrolytic solution containing carbon dioxide. The anode and the cathode are arranged in at least partial contact with the electrolytic solution. In the apparatus, a potential is applied to between the anode and the cathode, whereby carbon dioxide is reduced into a carbon material in the cathode, causing the flow of current.

[0018] Examples of the anode include, but are not limited to, Pt, conductive metal oxide, glassy carbon, and boron-doped diamond electrodes. The conductive metal oxide electrode may be, for example, a transparent conductive electrode, called ITO electrode, prepared by the film formation of a mixed oxide of indium and tin on glass, or an electrode, called DSA electrode (trademark of De Nora Permelec Ltd.), prepared by the film formation of an oxide of a platinum group metal such as ruthenium or iridium on a substrate of titanium or the like.

[0019] In a preferred embodiment, the anode can be a Pt electrode. Use of a Pt electrode as the anode permits stable electrolytic reduction at a lower cell voltage over a long time. A low cell voltage exerts effects that electric power required for the electrolytic reduction is lowered, and the environmental burden is more reduced.

[0020] Examples of the cathode include, but are not

limited to, electrodes of Ag, Cu, Ni, Pb, Hg, Ti, Bi, In, Sn, Cd, Au, Zn, Pd, Ga, Ge, Ni, Fe, Pt, Pd, Ru, Ti, Cr, Mo, W, V, Nb, Ta, and Zr, and alloys thereof, and electrodes of carbon materials such as glassy carbon, pyrolytic graphite, plastic formed carbon, and conductive diamond.

[0021] In a preferred embodiment, the cathode can be a Ag electrode. Use of a Ag electrode as the cathode permits stable electrolytic reduction at a lower cell voltage over a long time.

[0022] In a more preferred embodiment, the anode can be a Pt electrode, and the cathode can be a Ag electrode. Use of a Pt electrode as the anode and a Ag electrode as the cathode permits stable electrolytic reduction at a lower cell voltage over a long time, and the electrolytic reduction progresses more efficiently.

[0023] In a preferred embodiment, the anode and/or the cathode is a plate-shaped electrode. Preferably, the cathode is a plate-shaped electrode. More preferably, both the anode and the cathode are plate-shaped electrodes.

[0024] The electrolytic solution preferably comprises at least an ionic liquid. In the electrolytic solution comprising the ionic liquid, electrolytic reduction progresses efficiently at a lower temperature. In this context, the ionic liquid means an ionic substance that is in a molten state at least at 40°C, preferably at 25°C, and consists of a cationic moiety and an anionic moiety.

[0025] The ionic liquid can be an ionic liquid preferably having a melting point of ordinary temperature or lower and specifically having that of 25°C or lower, preferably 20°C or lower. Use of an ionic liquid having a melting point of ordinary temperature or lower permits efficient electrolytic reduction at ordinary temperature and eliminates the need of heating the electrolytic solution during electrolytic reduction.

[0026] The ionic liquid desirably has a wide potential window, i.e., high redox resistance. The electrolytic reduction can be efficiently carried out for a long time by using an ionic liquid that is stable against oxygen generation reaction in the anode and the reduction reaction of carbon dioxide in the cathode in the present manufacturing method.

[0027] The ionic liquid desirably has high carbon dioxide solubility. Use of the ionic liquid having high carbon dioxide solubility enables electrolytic reduction to be carried out with higher efficiency.

[0028] Examples of the ionic liquid include an imidazolium-based ionic liquid, an aromatic ionic liquid, a pyrrolidinium-based ionic liquid, an ammonium-based ionic liquid, a piperidinium-based ionic liquid, and a quaternary phosphonium-based ionic liquid.

[0029] Examples of the imidazolium-based ionic liquid include, but are not limited to, hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_6Im-NTf_2$), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-TFSI, $C_4C_4Im-NTf_2$), 1-hexyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide

($C_1C_1C_6Im-NTf_2$), 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_1C_4Im-NTf_2$), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_2Im-NTf_2$), 1-nonyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_8Im-NTf_2$), 1-nonyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_1C_8Im-NTf_2$), 1-propyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ($C_1C_1C_3Im-NTf_2$), 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide (EVI $m-NTf_2$), 1,2-dimethyl-1-propylimidazolium bis(trifluoromethanesulfonyl)imide (DMPI-TFSI), 1,2-dimethyl-1-propylimidazolium tris(trifluoromethylsulfonyl)imide (DMPI-Me), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI- BF_4), 1-ethyl-3-methylimidazolium chloride (EMI- Cl), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI), 1-ethyl-3-methylimidazolium bis(perfluoroethyl)sulfonyl)imide (EMI-BETI), 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (EMI-TfO), 1-ethyl-3-methylimidazolium trifluoroacetate (EMI-TA), 1-ethyl-3-methylimidazolium 2,3 hydrogen fluoride (EMI-F(HF) $_{2.3}$), 1-ethyl-3-methylimidazolium bis(fluorosulfonyl)imide (EMI-FSI), 1-ethyl-3-methylimidazolium hexafluorophosphate (EMI- PF_6), 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM- BF_4), 1-butyl-3-methylimidazolium trifluoroacetate (BMIM-TA), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM- PF_6), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-TFSI), 1-octyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (C8MI-TFSI), 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (CsMI-TFSI), 1,2-dimethyl-3-propylimidazolium bis(trifluoromethanesulfonyl)imide (DMPI-TFSI), and 1,2-dimethyl-3-propylimidazolium bismethide (DMPI-Me).

[0030] Examples of the aromatic ionic liquid include, but are not limited to, diphenylmethane diisocyanate bis(trifluoromethanesulfonyl)imide (MDI-TFSI).

[0031] Examples of the ammonium-based ionic liquid include, but are not limited to, N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate (DEME- BF_4), trimethylpropylammonium bis(trifluoromethanesulfonyl)imide (TMPA-TFSI), tetraethylammonium 2,2,2-trifluoro-N-(trifluoromethylsulfonyl)acetamide (TEA-(CF_3CO)(CF_3SO_2)N), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME- NTf_2), and N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(fluorosulfonyl)imide (DEME-FSI).

[0032] Examples of the pyrrolidinium-based ionic liquid include, but are not limited to, N-methyl-N-propylpyrrolidinium hexafluorophosphate ($P_{13}-PF_6$), N-methyl-N-propylpyrrolidinium bis(trifluoromethanesulfonyl)imide ($P_{13}-TFSI$), N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)imide ($P_{13}-FSI$), and N-methyl-N-methylpyrrolidinium bis(fluorosulfonyl)imide ($P_{14}-FSI$).

[0033] Examples of the piperidinium-based ionic liquid

include, but are not limited to, N-propyl-N-methylpiperidinium bis(trifluoromethanesulfonyl)imide (PMPip- $\text{CF}_3\text{SO}_2)_2\text{N}$) and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($\text{PP}_{13}\text{-TFSI}$).

[0034] Examples of the quaternary phosphonium-based ionic liquid include, but are not limited to, triethylpentyolphosphonium bis(trifluoromethanesulfonyl)imide ($\text{P}_{2225}\text{-TFSI}$), triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide ($\text{P}_{2228}\text{-TFSI}$), tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide ($\text{P}_{4441}\text{-TFSI}$), and triethylmethoxymethylphosphonium bis(trifluoromethanesulfonyl)imide ($\text{P}_{222(101)}\text{-TFSI}$).

[0035] In a preferred embodiment, the ionic liquid can be N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate (DEME- BF_4), N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI), N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($\text{PP}_{13}\text{-TFSI}$), 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-TFSI), or 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM- BF_4). The electrolytic reduction progresses efficiently at a lower temperature by using DEME- BF_4 , DEME-TFSI, $\text{PP}_{13}\text{-TFSI}$, BMIM-TFSI, or BMIM- BF_4 as the ionic liquid.

[0036] Only one of these ionic liquids may be used singly, or two or more thereof may be used in combination.

[0037] In one embodiment, the electrolytic solution consists of an ionic liquid.

[0038] In an alternative embodiment, the electrolytic solution can comprise a supporting electrolyte and other additives capable of increasing efficiency of electrolytic reduction, in addition to the ionic liquid.

[0039] In one embodiment, the electrolytic solution consists of an ionic liquid and a supporting electrolyte. The electrolytic reduction progresses efficiently at a lower temperature by using the electrolytic solution consisting of an ionic liquid and a supporting electrolyte.

[0040] The supporting electrolyte is not limited and preferably contains a cation having a low or equivalent standard electrode potential that does not interfere with the electrolytic reduction of carbon dioxide or the electrolytic reduction of H_2O .

[0041] Examples of the supporting electrolyte include, but are not limited to, KHCO_3 , KHPO_4 , LiBF_4 , LiPF_6 , LiClO_4 , LiAsF_6 , LiTf , LiTFSI , LiFSI , K_2CO_3 , Li_2CO_3 , Na_2CO_3 , and NaHCO_3 .

[0042] In a preferred embodiment, the supporting electrolyte can be LiBF_4 , LiPF_6 , LiTFSI , or LiFSI . The electrolytic reduction progresses efficiently at a lower temperature by using LiBF_4 , LiPF_6 , LiTFSI , or LiFSI as the supporting electrolyte.

[0043] Only one of these supporting electrolytes may be used singly, or two or more thereof may be used in combination.

[0044] In a preferred embodiment, the combination of the ionic liquid and the supporting electrolyte can be a combination of DEME- BF_4 or DEME-TFSI and LiBF_4 , more preferably a combination of DEME- BF_4 and LiBF_4 .

[0045] The concentration of the supporting electrolyte to be added to the ionic liquid in the electrolytic solution can be preferably from 0.01 mol/L to a saturated concentration, more preferably 0.02 to 1.00 mol/L, further preferably 0.05 to 0.75 mol/L, still further preferably 0.10 to 0.50 mol/L. When the concentration of the supporting electrolyte to be added to the ionic liquid falls within the range described above, the electrolytic reduction progresses more efficiently.

[0046] In a preferred embodiment, the electrolytic solution does not substantially contain a protic solvent such as water. When the electrolytic solution does not contain a protic solvent such as water, the electrolytic reduction progresses efficiently because it is not accompanied by generation of hydrogen due to electrolysis of water or the like. Examples of the protic solvent include alcohols, formic acid, and hydrogen fluoride.

[0047] The concentration of carbon dioxide in the electrolytic solution is not limited and is preferably a high concentration. The concentration can be, for example, a saturated concentration.

[0048] Examples of the method for dissolving carbon dioxide in the electrolytic solution include, but are not limited to, the bubbling of carbon dioxide into the electrolytic solution, a method of rendering carbon dioxide saturated in an electrolyzer containing the electrolytic solution, stirring using a stirring apparatus, stirring by ultrasonic application, and use of a flow electrolysis cell.

[0049] In the electrolytic reduction method of the present disclosure, carbon dioxide may be used in combination with an additional gas. Examples of the gas to be used in combination include argon, nitrogen, hydrogen, and water vapor.

[0050] The temperature of the electrolytic solution in performing the electrolytic reduction can be preferably 0 to 100°C , more preferably 0 to 80°C , further preferably 10 to 50°C , still further preferably 20 to 40°C . In the electrolytic reduction method of the present disclosure, the electrolytic reduction progresses efficiently even at the temperature of the electrolytic solution set to such a relatively low temperature as described above. Thus, an energy cost can be reduced.

[0051] The pressure in performing the electrolytic reduction can be preferably atmospheric pressure to 0.5 MPa, for example, 0.1 MPa to 0.5 MPa, more preferably 0.1 MPa to 0.3 MPa, further preferably 0.1 MPa to 0.2 MPa. In the electrolytic reduction method of the present disclosure, the electrolytic reduction progresses efficiently even under no pressure or small pressure. Thus, an energy cost can be reduced.

[0052] In a preferred embodiment, the electrolytic reduction is preferably carried out at 20 to 40°C and 0.09 MPa to 0.11 MPa, more preferably at ordinary temperature and normal pressure.

[0053] The potential of the cathode in performing the electrolytic reduction can be preferably -5.0 V to -0.5 V, more preferably -3.5 V to -0.5 V. The potential is a potential when a Ag^+/Ag electrode is used as a reference

electrode. When the potential of the cathode falls within the range described above, the electrolytic reduction progresses more efficiently.

[0054] Examples of the carbon material obtained in the method for manufacturing a carbon material according to the present disclosure include diamond, graphite, glassy carbon, amorphous carbon, carbon nanotube, carbon nanohorn, and graphene.

[0055] The carbon material is preferably diamond or glassy carbon, more preferably diamond.

[0056] In the method for manufacturing a carbon material according to the present disclosure, carbon dioxide can be selectively electrolytically reduced into a carbon material by adjusting a potential to be applied to between the anode and the cathode.

[0057] Thus, the present disclosure also provides an electrolytic reduction method comprising electrolytically reducing carbon dioxide in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein carbon dioxide is selectively electrolytically reduced into a carbon material selected from the group consisting of diamond, graphite, glassy carbon, amorphous carbon, carbon nanotube, carbon nanohorn, and graphene by a potential to be applied to between the anode and the cathode.

[0058] For example, when DEME-BF₄ is used as the ionic liquid, and LiBF₄ is added at a concentration of 0.2 mol/L as the supporting electrolyte, diamond is produced at room temperature by setting the potential to -5.0 V to -2.4 V. When P₂₂₂₅-TFSI is used as the ionic liquid, and a supporting electrolyte is not added, diamond is produced at room temperature by setting the potential to -3.7 V to -2.6 V.

[0059] As described above, in the method for manufacturing a carbon material of carbon dioxide according to the present disclosure, electrolytic reduction of carbon dioxide can be carried out efficiently at a relatively low temperature. Particularly, by adding the ionic liquid to the electrolytic solution, the potential window is enlarged, and by controlling a potential to be applied, carbon dioxide can be electrolytically reduced into a carbon material more efficiently. Besides, since the ionic liquid has a low melting temperature and high stability, safe and stable electrolytic reduction can be carried out at a low temperature, and an energy cost can be reduced. By controlling a potential to be applied, a desired carbon material can also be obtained.

[0060] Although the present invention is described above, the present invention is not limited by those described above. Various changes or modifications can be made therein without departing from the spirit of the present invention.

Examples

[0061] Hereinafter, the present invention will be specifically described with reference to Examples given below. However, the present invention is not limited by

these Examples.

[0062] Figure 1 schematically shows an experiment apparatus used in the present Examples. The experiment apparatus has electrolyzer 1, carbon dioxide supply pipe 2, working electrode WE which is a cathode, counter electrode CE which is an anode, reference electrode RE, and exhaust pipe 3. The electrolyzer 1 has cell body 11 and lid 12 which closes the upper opening of the cell body 11. The working electrode WE is a Ag plate electrode, and connected to conductor wire 4 made of Ni. The counter electrode CE is a Pt plate electrode and connected to conductor wire 4 made of Ni. The reference electrode RE is a Ag⁺/Ag electrode and connected to conductor wire 4 made of Ni. The electrolyzer 1 contains electrolytic solution 7, and the working electrode WE, the counter electrode CE, and the reference electrode RE are fixed in a state dipped in the electrolytic solution 7. The working electrode WE, the reference electrode RE, and the counter electrode CE were connected to a potentiostat/galvanostat apparatus (manufactured by BioLogic Science Instruments Ltd.) through the conductor wire 4.

(Example 1)

[0063] An ionic liquid DEME-BF₄ was mixed with a supporting electrolyte LiBF₄ at a ratio of 0.2 mol/L to obtain electrolytic solution A. The obtained electrolytic solution A was added into the electrolyzer 1 in such an amount that each electrode was dipped in the electrolytic solution A, and the gas supply pipe 2 and the exhaust pipe 3 were not in contact with the electrolytic solution A. In this state, carbon dioxide was supplied into the electrolyzer 1 from the gas supply pipe 2 at a gas pressure of 0.1 MPa to produce a carbon dioxide-saturated atmosphere inside the electrolyzer 1. Subsequently, the reduction behavior of carbon dioxide was observed by applying a potential to between the working electrode WE and the counter electrode CE at a scanning rate of 10 mV/s by cyclic voltammetry, and measuring a current density.

(Comparative Example 1)

[0064] The same operation as in Example 1 was performed except that Ar was used instead of carbon dioxide.

[0065] The results of Example 1 and Comparative Example 1 are shown in the graph of Figure 2. In the graph, the solid line depicts the results of Example 1, and the broken line depicts the results of Comparative Example 1. From the results in Figure 2, reduction current in the carbon dioxide atmosphere in Example 1 was confirmed to rise from -2.5 V. That is to say, electrolytic reduction of carbon dioxide was confirmed to progress at a potential lower than -2.5 V in the electrolytic solution A.

(Examples 2 and 3)

[0066] Change in current density was measured in the

same manner as in Example 1 except that the potential of the Ag electrode serving as the cathode was cathodically polarized to constant potentials of -2.45 V and -4.86 V. The results are shown in Figure 3.

[0067] From the results in Figure 3, in each of the cases where the Ag electrode potential was cathodically polarized to -2.45 V and -4.86 V, steady transition of a reduction current value was confirmed, and the reduction reaction of carbon dioxide was confirmed to stably progress at each potential.

[0068] In Examples 2 and 3, the surface state of each Ag electrode was subjected to Raman spectroscopy after electrolytic reduction was carried out for 1 hour. The results are shown in Figure 4.

[0069] As shown in Figure 4, Raman peak at 1332 cm^{-1} attributable to diamond, Raman band at approximately 1580 cm^{-1} attributable to G-band of carbon, and Raman band at approximately 1360 cm^{-1} attributable to D-band of carbon were confirmed. That is to say, it was confirmed that carbon dioxide had been reduced by the electrolytic reduction, and a carbon material including diamond had been deposited.

(Example 4)

[0070] Change in current density was measured in the same manner as in Example 1 except that electrolytic solution B composed of only an ionic liquid $\text{P}_{2225}\text{-TFSI}$ was added into the electrolyzer 1 of the electrolysis apparatus.

(Comparative Example 2)

[0071] The same operation as in Example 4 was performed except that Ar was used instead of carbon dioxide.

[0072] The results of Example 4 and Comparative Example 2 are shown in Figure 5. In the graph, the solid line depicts the results of Example 4, and the broken line depicts the results of Comparative Example 2. From the results in Figure 5, electrolytic reduction of carbon dioxide was confirmed to progress within the range of the potential window of the ionic liquid $\text{P}_{2225}\text{-TFSI}$. That is to say, reduction current in the inert Ar atmosphere using $\text{P}_{2225}\text{-TFSI}$ rises at approximately -3.4 V, whereas in the carbon dioxide atmosphere, reduction current was confirmed to rise from approximately -2.8 V that is a potential higher than the above potential. The results indicate that the reduction of carbon dioxide occurs without being influenced by the reductive decomposition of the $\text{P}_{2225}\text{-TFSI}$ itself.

(Examples 5 to 9)

[0073] Change in current density was measured in the same manner as in Example 4 except that the potential of the Ag electrode serving as the cathode was cathodically polarized to constant potentials of -2.60 V, -3.00 V,

-3.15 V, -3.25 V, and -3.70 V. The results are shown in Figures 6 to 10.

[0074] From the results in Figures 6 to 10, in each of the cases where the Ag electrode potential was cathodically polarized to -2.60 V, -3.00 V, -3.15 V, -3.25 V, and -3.70 V, steady transition of a reduction current value was confirmed, and the reduction reaction of carbon dioxide was confirmed to stably progress at each potential.

[0075] In Examples 5 to 9, the surface state of each Ag electrode was subjected to Raman spectroscopy after electrolytic reduction was carried out for 1 hour. The results are shown in Figures 11 to 15.

[0076] As shown in Figures 11 to 16, Raman bands derived from diamond, and G-band and D-band of carbon were confirmed at each electrolysis potential, and from this, it was confirmed that in the range of at least -3.7 V to -2.6 V, a carbon material including diamond had been deposited by the reduction of carbon dioxide.

(Example 10)

[0077] The same operations as in Examples 4 to 9 were each performed except that electrolytic solution H composed of triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide ($\text{P}_{2228}\text{-TFSI}$) was added instead of $\text{P}_{2225}\text{-TFSI}$.

[0078] From the results, CO_2 was confirmed to be reduced in the range of -3.2 V to -0.7 V in the case of using the electrolytic solution H.

(Example 11)

[0079] The same operations as in Examples 4 to 9 were each performed except that electrolytic solution I composed of tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide ($\text{P}_{4441}\text{-TFSI}$) was added instead of $\text{P}_{2225}\text{-TFSI}$.

[0080] From the results, CO_2 was confirmed to be reduced in the range of -3.2 V to -0.5 V in the case of using the electrolytic solution I.

(Example 12 and Comparative Example 3)

[0081] The same operations as in Example 1 and Comparative Example 1 were each performed except that N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide ($\text{PP}_{13}\text{-TFSI}$) was used instead of DEME-BF_4 . The results are shown in the graph of Figure 16. The solid line depicts the results of Example 12, and the broken line depicts the results of Comparative Example 3.

(Example 13 and Comparative Example 4)

[0082] The same operations as in Example 1 and Comparative Example 1 were each performed except that 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BMIM-TFSI) was used instead of DEME-BF_4 . The results are shown in the graph of Figure 17. The

solid line depicts the results of Example 13, and the broken line depicts the results of Comparative Example 4.

(Example 14 and Comparative Example 5)

[0083] The same operations as in Example 1 and Comparative Example 1 were each performed except that 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM-BF₄) was used instead of DEME-BF₄. The results are shown in the graph of Figure 18. The solid line depicts the results of Example 14, and the broken line depicts the results of Comparative Example 5.

[0084] From the results in Figures 16 to 18, reduction current in the carbon dioxide atmosphere was confirmed to rise in each of Examples 12 to 14. That is to say, electrolytic reduction of carbon dioxide was confirmed to progress at a potential lower than the predetermined potential.

(Example 15)

[0085] An ionic liquid DEME-BF₄ was mixed with each of supporting electrolytes LiBF₄, LiPF₆, LiTFSI, and LiFSI at a ratio of 0.2 mol/L to obtain electrolytic solutions A1 to A4. As for each of the electrolytic solutions, change in current density was measured in the same manner as in Example 1 except that the obtained electrolytic solutions A1 to A4 were each used. From the results, CO₂ was confirmed to be reduced in the range of -3.5 V to -0.8 V in the case of using each of the electrolytic solutions A1 to A4.

(Example 16)

[0086] Electrolytic solutions B1 to B4 were obtained in the same manner as in Example 15 except that the concentration of each of the supporting electrolytes was set to 0.4 mol/L, and as for each of the electrolytic solutions, change in current density was measured. From the results, CO₂ was confirmed to be reduced in the range of -3.5 V to -0.6 V in the case of using each of the electrolytic solutions B1 to B4.

(Example 17)

[0087] Electrolytic solutions C1 to C4 were obtained in the same manner as in Example 15 except that the concentration of each of the supporting electrolytes was set to 0.6 mol/L, and as for each of the electrolytic solutions, change in current density was measured. From the results, CO₂ was confirmed to be reduced in the range of -3.5 V to -0.6 V in the case of using each of the electrolytic solutions C1 to C4.

(Example 18)

[0088] Electrolytic solutions D1 to D4 were obtained in the same manner as in Example 15 except that the con-

centration of each of the supporting electrolytes was set to 0.8 mol/L, and as for each of the electrolytic solutions, change in current density was measured. From the results, CO₂ was confirmed to be reduced in the range of -3.6 V to -1.0 V in the case of using each of the electrolytic solutions D1 to D4.

(Example 19)

[0089] Electrolytic solutions E1 to E4 were obtained in the same manner as in Example 15 except that the concentration of each of the supporting electrolytes was set to 1.0 mol/L, and as for each of the electrolytic solutions, change in current density was measured. From the results, CO₂ was confirmed to be reduced in the range of -3.6 V to -1.0 V in the case of using each of the electrolytic solutions D1 to D4.

(Example 20)

[0090] Electrolytic solutions F1 to F4 were obtained in the same manner as in Example 15 except that the concentration of each of the supporting electrolytes was set to 1.2 mol/L, and as for each of the electrolytic solutions, change in current density was measured. From the results, CO₂ was confirmed to be reduced in the range of -3.6 V to -0.8 V in the case of using each of the electrolytic solutions F1 to F4.

(Example 21)

[0091] Electrolytic solutions G1 to G4 were obtained in the same manner as in Example 15 except that the concentration of each of the supporting electrolytes was set to 1.4 mol/L, and as for each of the electrolytic solutions, change in current density was measured. From the results, CO₂ was confirmed to be reduced in the range of -3.6 V to -1.0 V in the case of using each of the electrolytic solutions G1 to G4.

Industrial Applicability

[0092] The electrolytic reduction method of the present disclosure can convert carbon dioxide responsible for global warming, etc. into useful carbon materials and as such, is useful in various fields, particularly, in the environmental field.

Reference Signs List

[0093]

- 1 Electrolyzer
- 2 Gas supply pipe
- 3 Exhaust pipe
- 4 Conductor wire
- 7 Electrolytic solution
- 11 Cell body

12 Lid

Claims

1. A method for manufacturing diamond, comprising electrolytically reducing carbon dioxide into diamond to obtain diamond in an electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein the electrolytic solution comprises an ionic liquid.

2. The method for manufacturing a carbon material according to claim 1, wherein:

the anode is a Pt electrode, and
the cathode is an Ag electrode.

3. The method for manufacturing a carbon material according to claim 1 or 2, wherein the ionic liquid is an imidazolium-based ionic liquid, an aromatic ionic liquid, a pyrrolidinium-based ionic liquid, an ammonium-based ionic liquid, a piperidinium-based ionic liquid, or a quaternary phosphonium-based ionic liquid.

4. The method for manufacturing a carbon material according to claim 1 or 2, wherein the ionic liquid is N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate, N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide, N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, 1-butyl-3-methylimidazolium tetrafluoroborate, triethylpentylophosphonium bis(trifluoromethanesulfonyl)imide, triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide, or tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide.

5. The method for manufacturing a carbon material according to any one of claims 1 to 4, wherein the electrolytic solution comprises a supporting electrolyte.

6. The electrolytic reduction method according to any one of claims 1 to 5, wherein the supporting electrolyte is KHCO_3 , KH_2PO_4 , LiBF_4 , LiPF_6 , LiClO_4 , LiAsF_6 , LiTf , LiTFSI , LiFSI , K_2CO_3 , Li_2CO_3 , Na_2CO_3 , or NaHCO_3 .

7. The electrolytic reduction method according to claim 5 or 6, wherein the supporting electrolyte is LiBF_4 , LiPF_6 , LiTFSI , or LiFSI .

8. The electrolytic reduction method according to any one of claims 5 to 7, wherein a concentration of the supporting electrolyte contained in the ionic liquid is from 0.01 mol/L to a saturated concentration.

9. The electrolytic reduction method according to any one of claims 1 to 8, wherein the electrolytic reduction apparatus further comprises a reference electrode, the reference electrode is a Ag^+/Ag electrode, and a potential of the cathode is -5.0 V to -0.5 V.

10. The electrolytic reduction method according to any one of claims 1 to 9, wherein a temperature of the electrolytic solution is 0 to 100°C.

11. The electrolytic reduction method according to any one of claims 1 to 10, wherein the electrolytic reduction is performed at ordinary temperature and normal pressure.

12. An electrolytic reduction apparatus having an anode, a cathode, and an electrolytic solution containing carbon dioxide, wherein:

the electrolytic solution comprises an ionic liquid selected from an imidazolium-based ionic liquid, an aromatic ionic liquid, a pyrrolidinium-based ionic liquid, an ammonium-based ionic liquid, a piperidinium-based ionic liquid, and a quaternary phosphonium-based ionic liquid, and carbon dioxide in the electrolytic solution is reduced into diamond.

13. The electrolytic reduction apparatus according to claim 12, wherein the anode is a Pt electrode, and the cathode is a Ag electrode.

14. The electrolytic reduction apparatus according to claim 12 or 13, wherein the ionic liquid is N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium tetrafluoroborate, N,N-diethyl-N-methyl-N-(2-methoxyethyl)ammonium bis(trifluoromethanesulfonyl)imide, N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide, 1-butyl-3-methylimidazolium tetrafluoroborate, triethylpentylophosphonium bis(trifluoromethanesulfonyl)imide, triethyloctylphosphonium bis(trifluoromethanesulfonyl)imide, or tributylmethylphosphonium bis(trifluoromethanesulfonyl)imide.

15. The electrolytic reduction apparatus according to any one of claims 12 to 14, wherein the electrolytic solution comprises a supporting electrolyte.

16. The electrolytic reduction apparatus according to claim 15, wherein the supporting electrolyte is KHCO_3 , KH_2PO_4 , LiBF_4 , LiPF_6 , LiClO_4 , LiAsF_6 , LiTf , LiTFSI , LiFSI , K_2CO_3 , Li_2CO_3 , Na_2CO_3 , or NaHCO_3 .

17. The electrolytic reduction apparatus according to claim 15 or 16, wherein the supporting electrolyte is LiBF_4 , LiPF_6 , LiTFSI , or LiFSI .

18. The electrolytic reduction apparatus according to any one of claims 15 to 17, wherein a concentration of the supporting electrolyte contained in the ionic liquid is from 0.01 mol/L to a saturated concentration.

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Fig.1

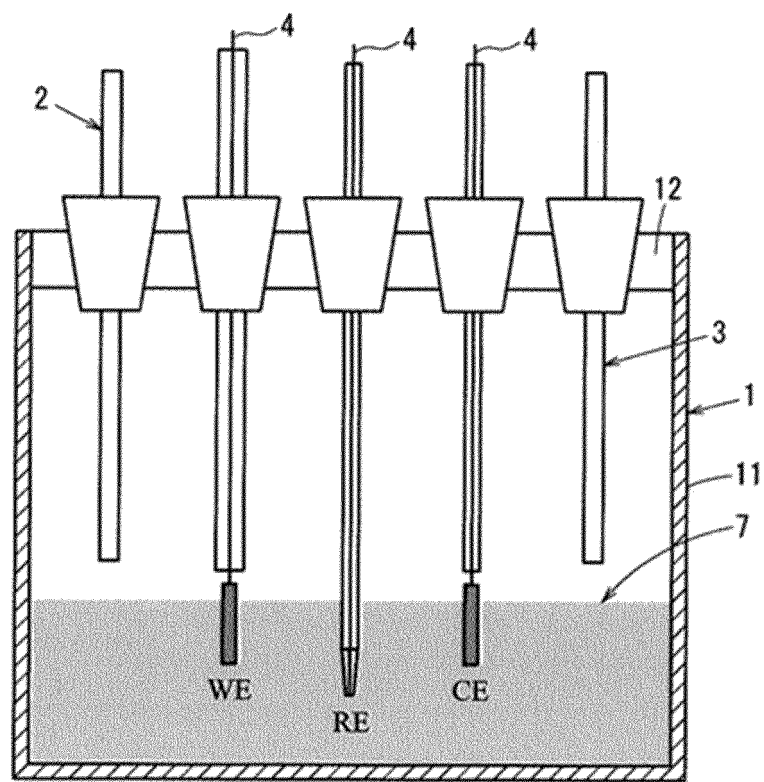


Fig.2

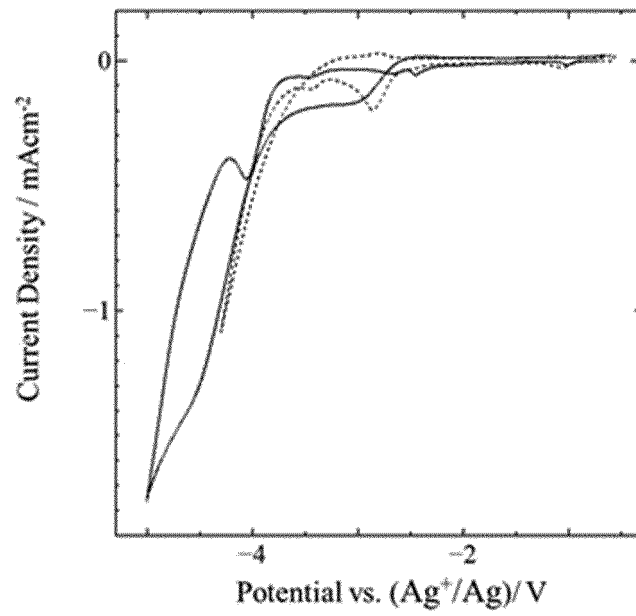


Fig.3

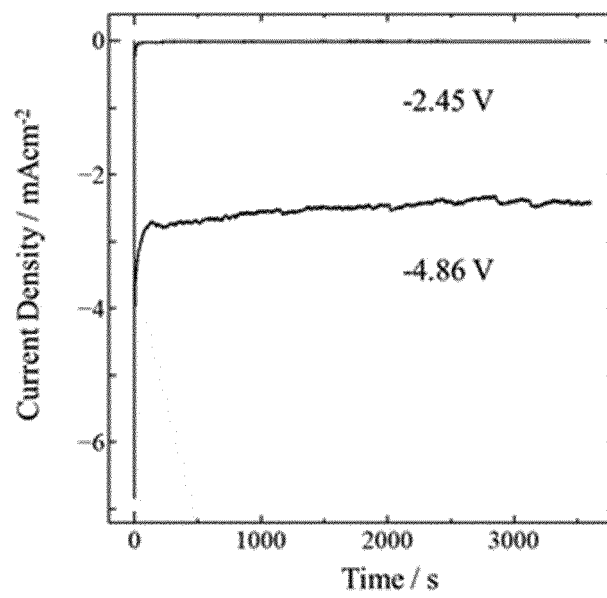


Fig.4

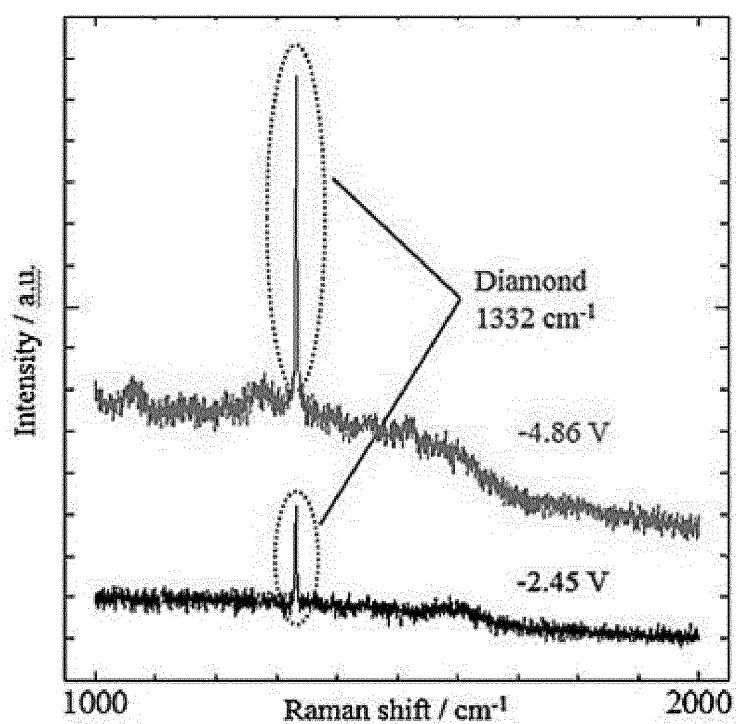


Fig.5

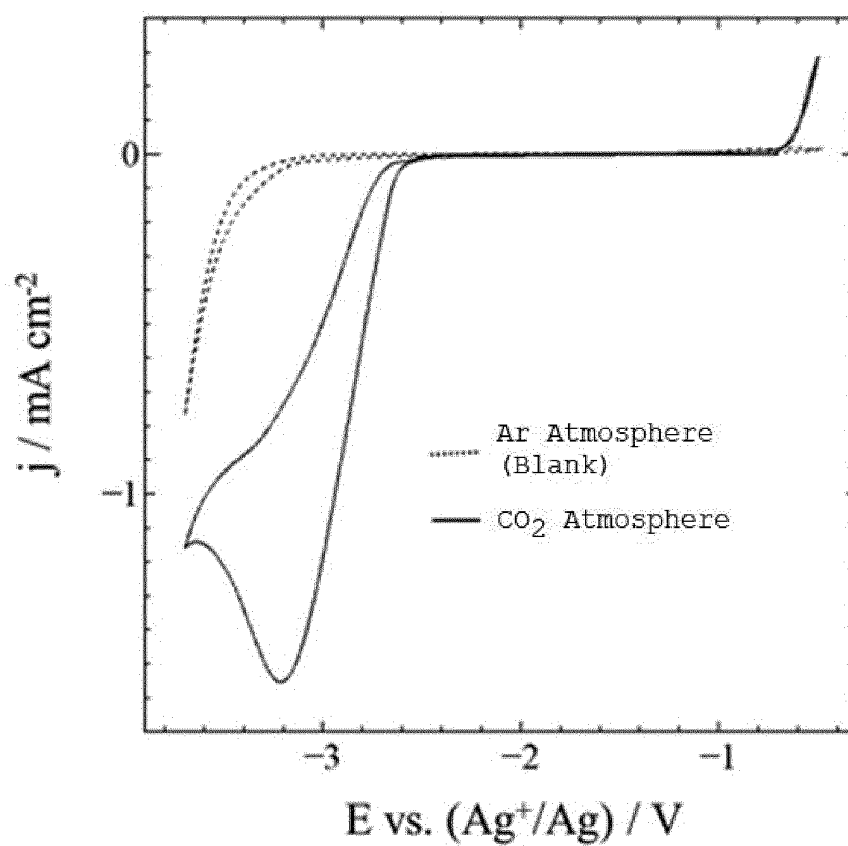


Fig.6

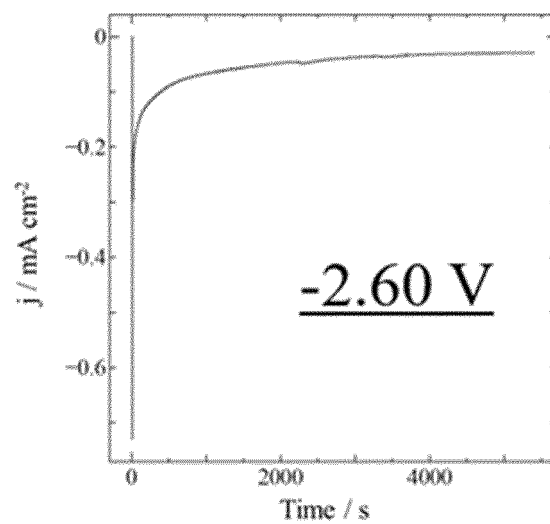


Fig.7

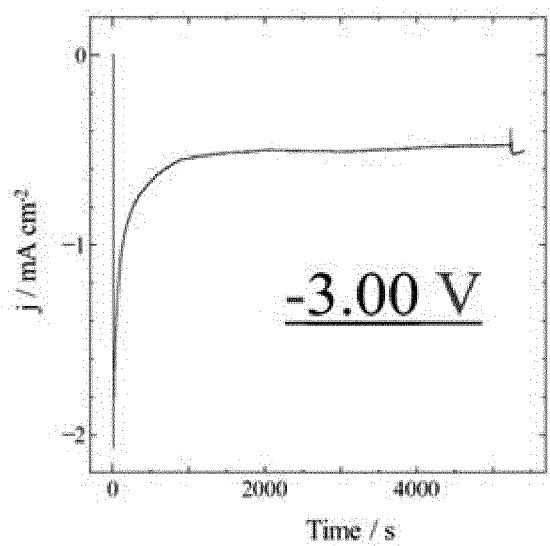


Fig.8

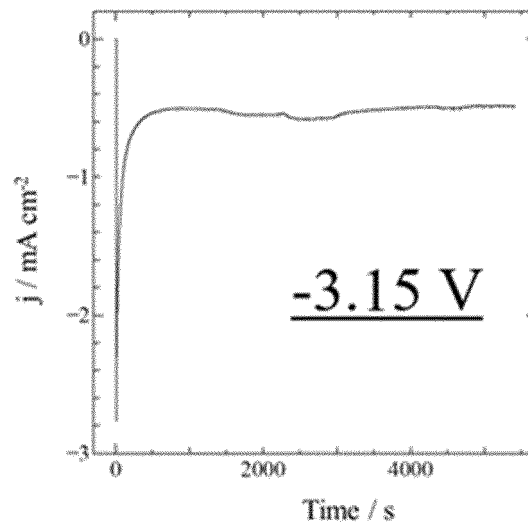


Fig.9

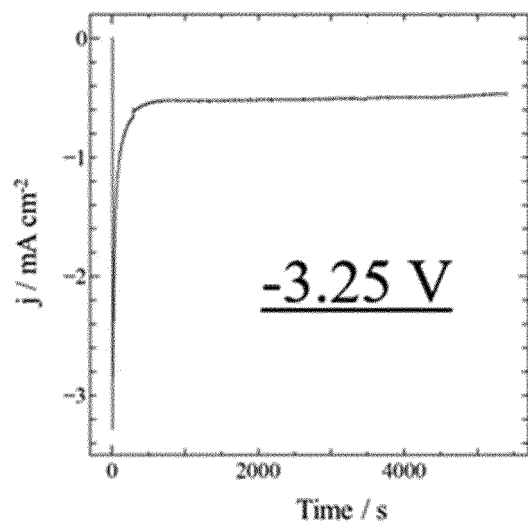


Fig.10

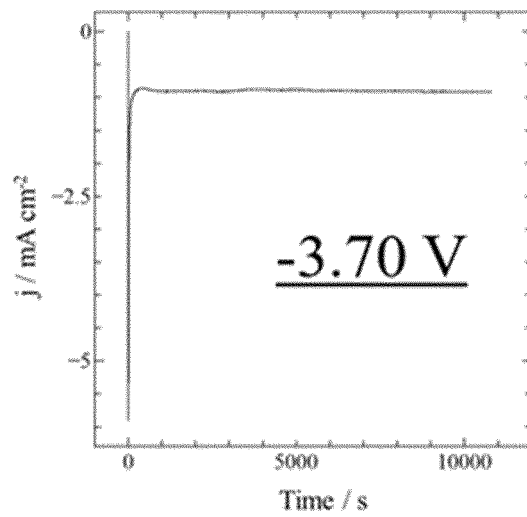


Fig.11

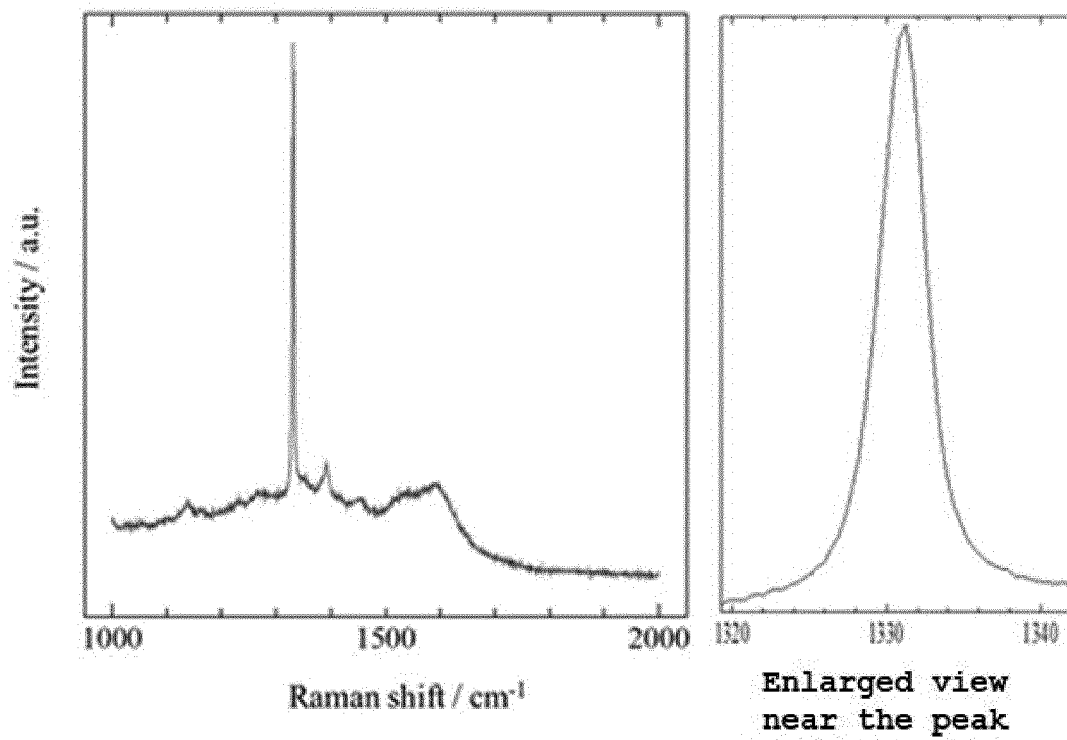


Fig.12

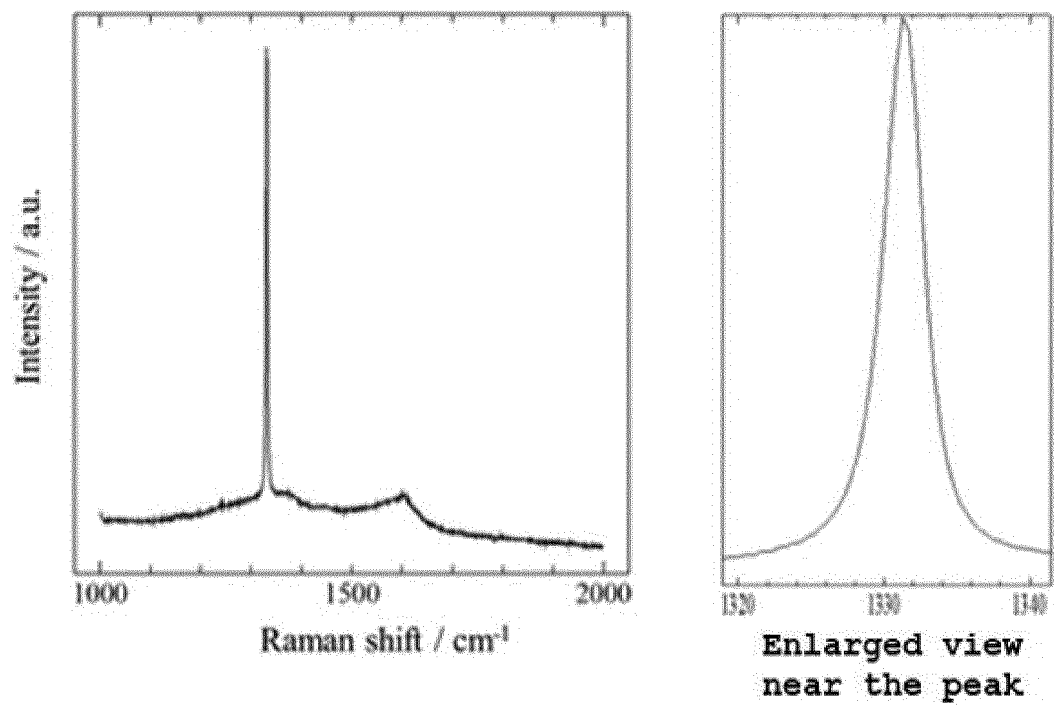


Fig.13

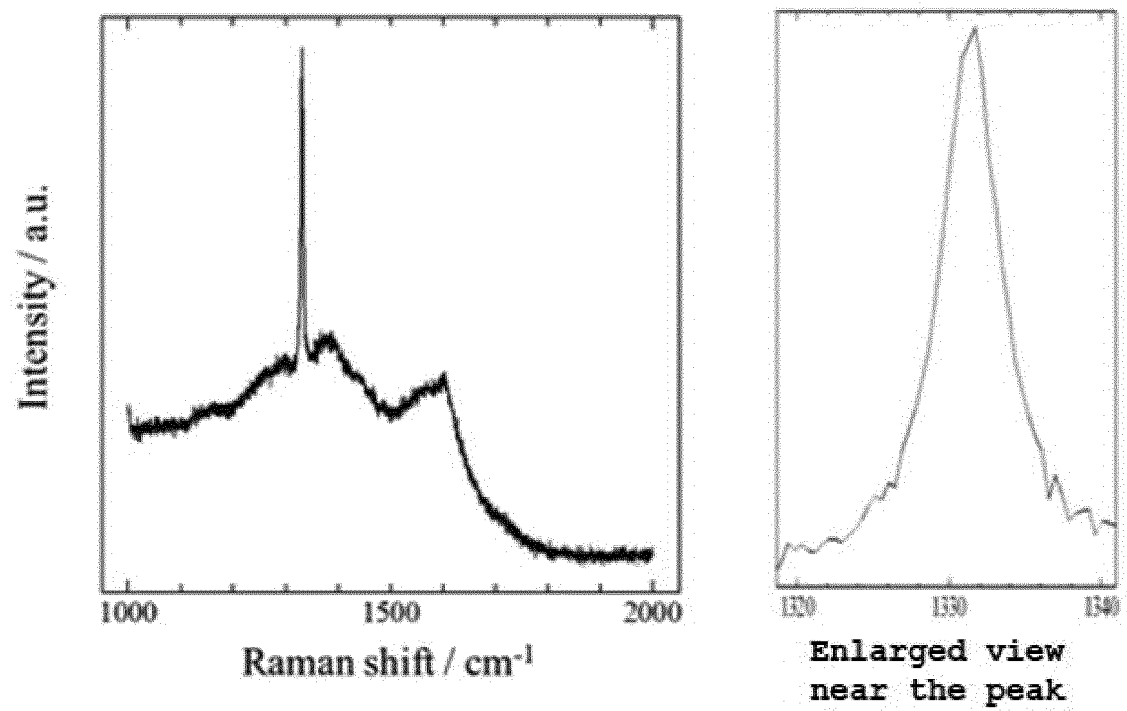


Fig.14

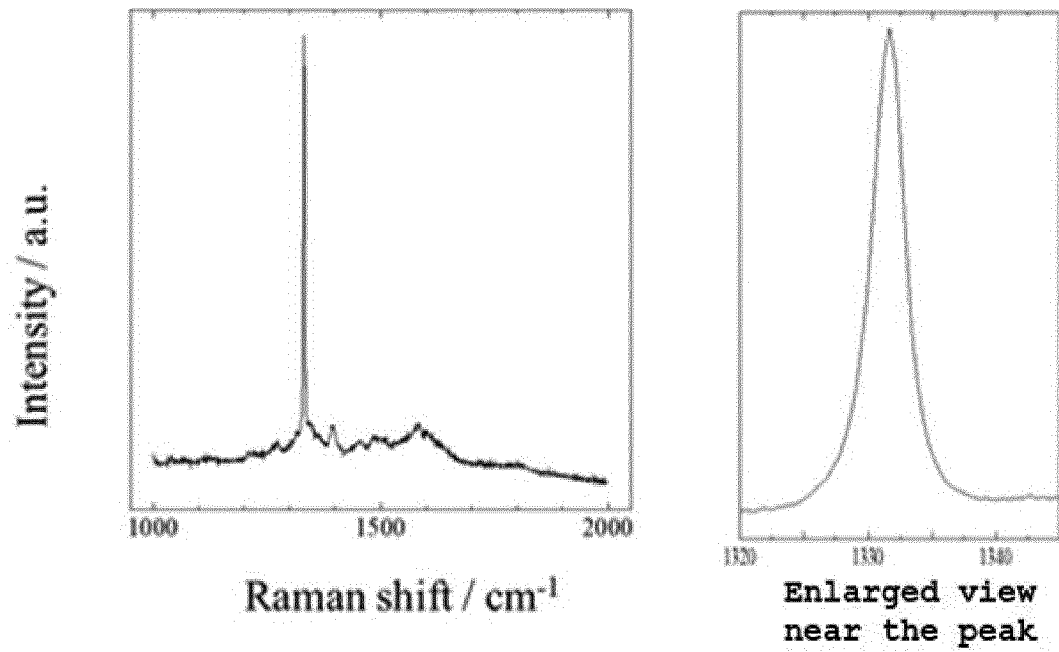


Fig.15

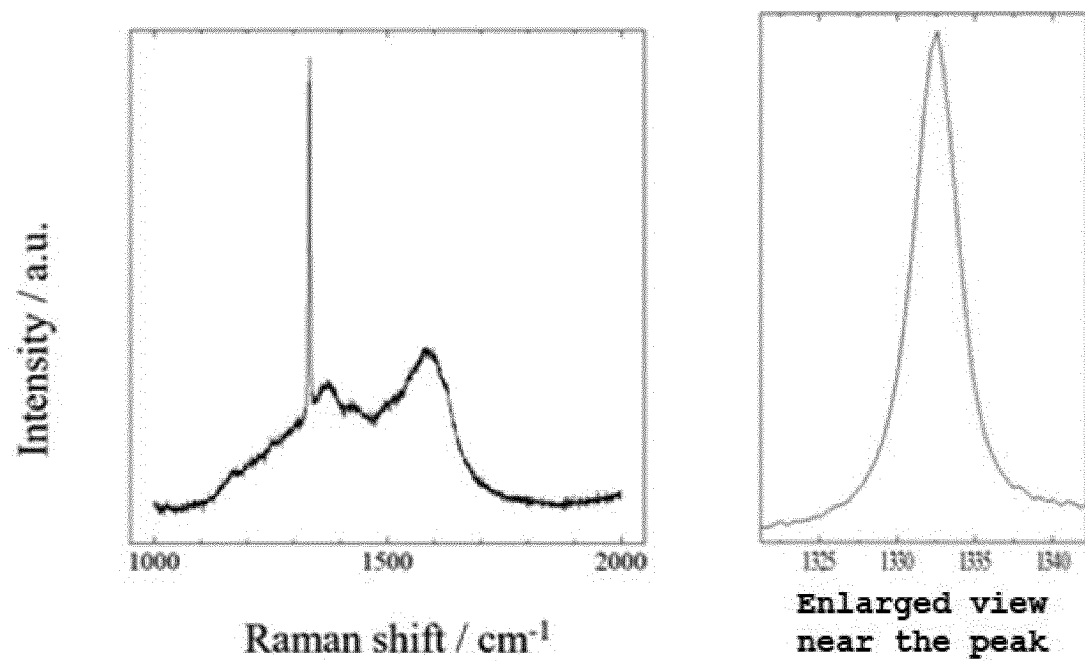


Fig.16

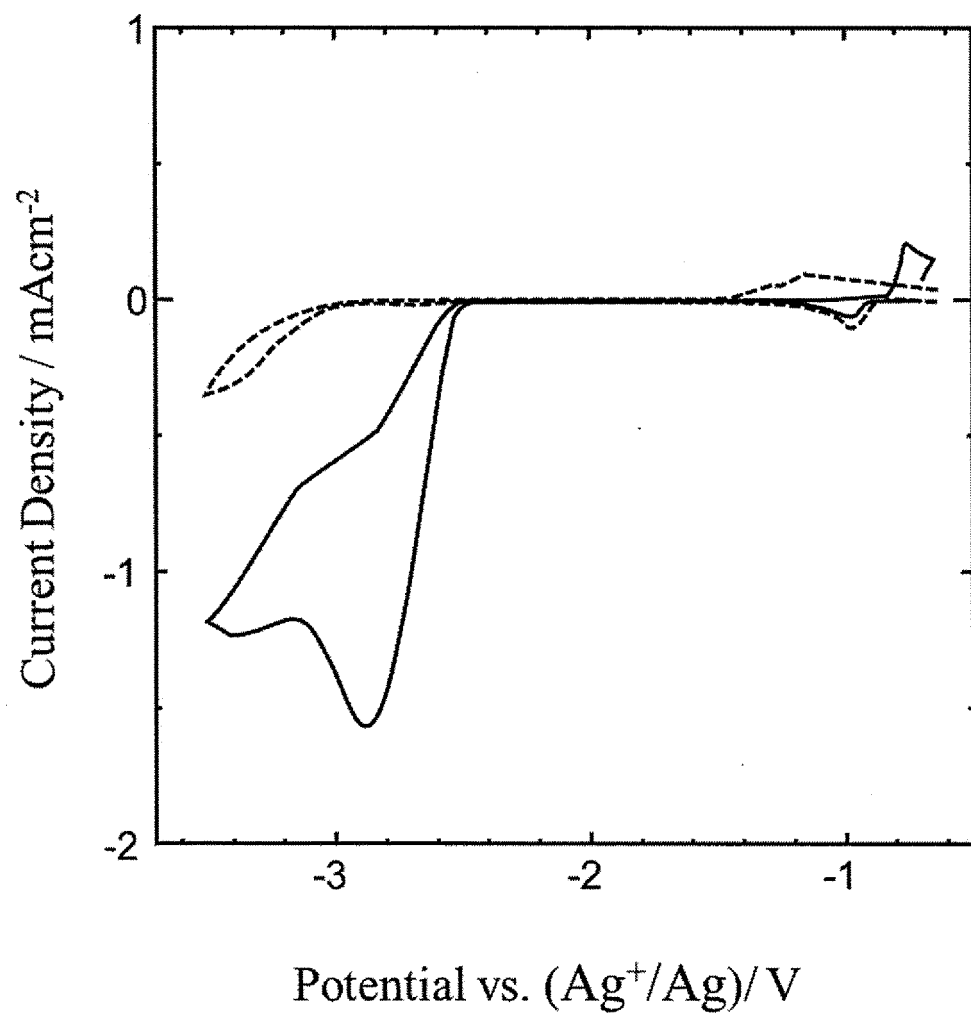


Fig.17

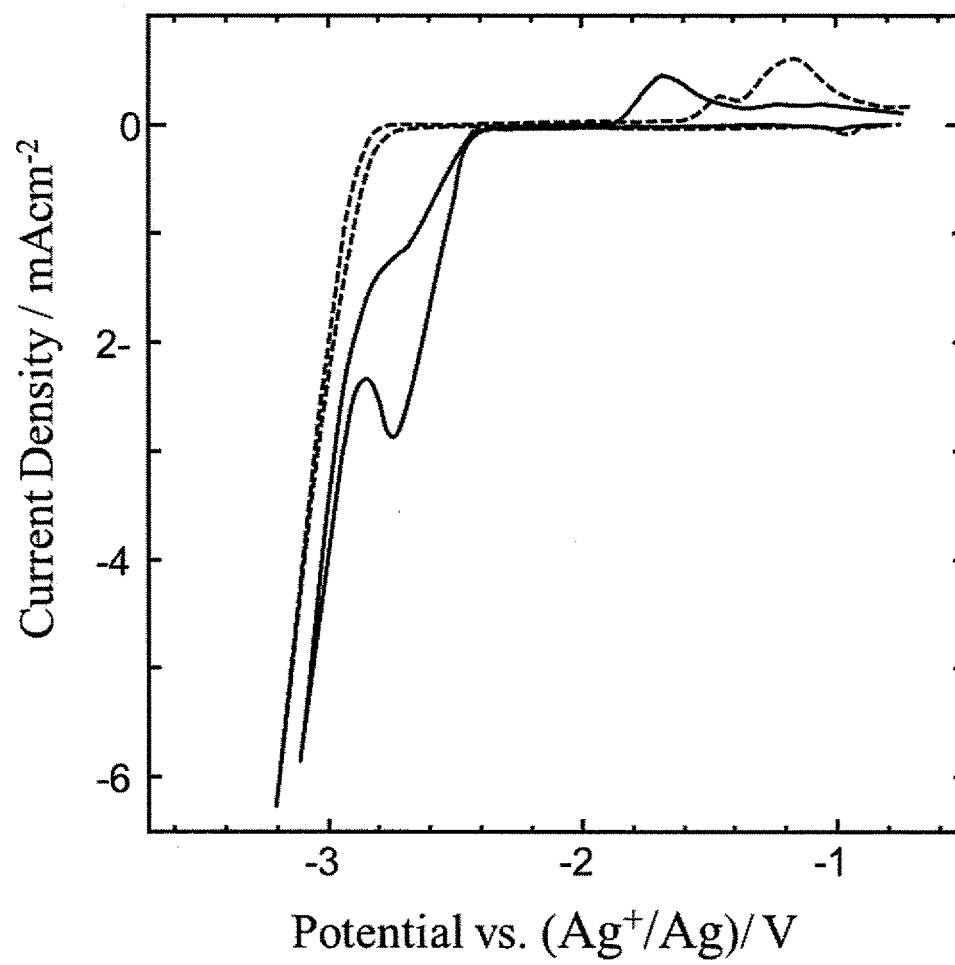
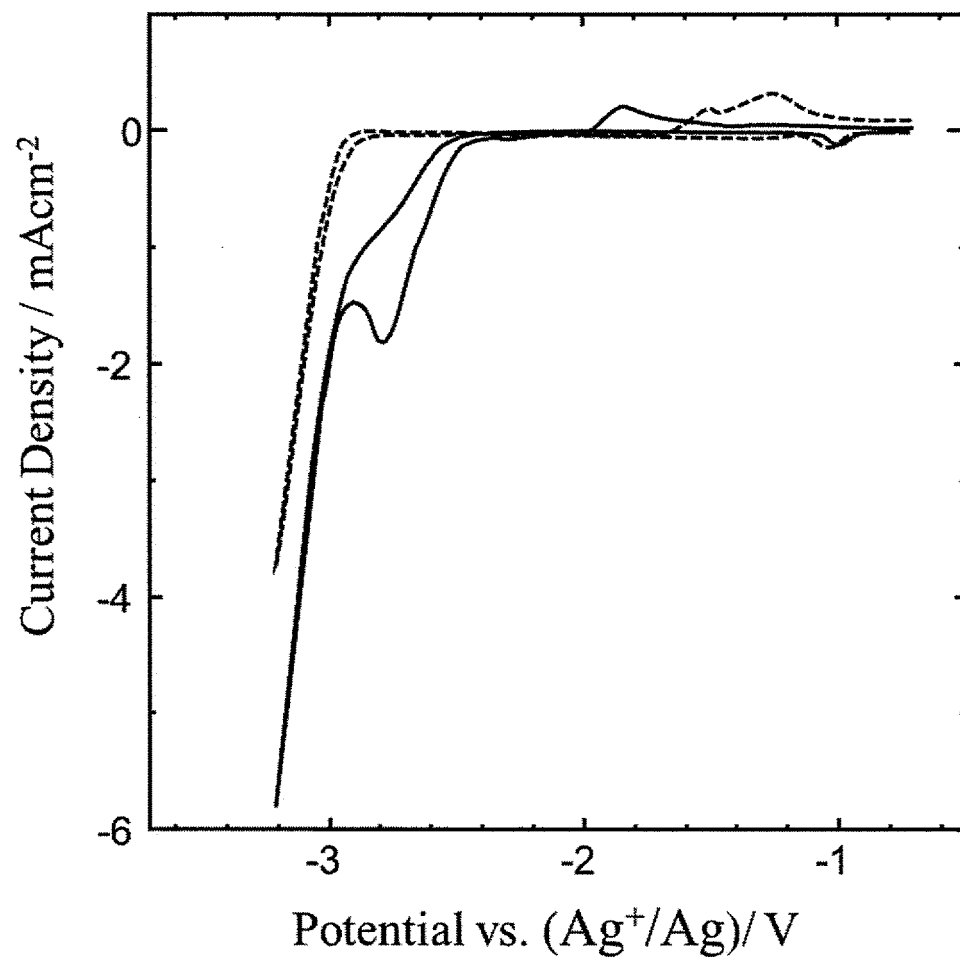


Fig.18



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2022/005734

A. CLASSIFICATION OF SUBJECT MATTER <i>C25B 1/135</i> (2021.01)i; <i>C25B 9/00</i> (2021.01)i; <i>C25B 11/04</i> (2021.01)i; <i>C25B 15/02</i> (2021.01)i FI: C25B1/135; C25B9/00 Z; C25B11/04; C25B15/02 According to International Patent Classification (IPC) or to both national classification and IPC																		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C25B1/135; C25B9/00; C25B11/04; C25B15/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2022 Registered utility model specifications of Japan 1996-2022 Published registered utility model applications of Japan 1994-2022 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																		
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>Preliminary Study of CO₂ Electrolysis in Ionic Liquid. 49th International Conference on Environmental Systems, 2019 pp. 2-6</td> <td>12-18</td> </tr> <tr> <td>Y</td> <td></td> <td>1-11</td> </tr> <tr> <td>Y</td> <td>JP 2016-89230 A (DOSHISHA) 23 May 2016 (2016-05-23) claims</td> <td>1-11</td> </tr> <tr> <td>Y</td> <td>US 2014/0202874 A1 (SARATOGA ENERGY RESEARCH PARTNERS, LLC) 24 July 2014 (2014-07-24) paragraphs [0020], [0063]</td> <td>1-11</td> </tr> <tr> <td>A</td> <td>CO₂ Electrorreduction in Ionic Liquids, frontiers in Chemistry, 2019 pp. 1-8</td> <td>1-18</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	Preliminary Study of CO ₂ Electrolysis in Ionic Liquid. 49th International Conference on Environmental Systems, 2019 pp. 2-6	12-18	Y		1-11	Y	JP 2016-89230 A (DOSHISHA) 23 May 2016 (2016-05-23) claims	1-11	Y	US 2014/0202874 A1 (SARATOGA ENERGY RESEARCH PARTNERS, LLC) 24 July 2014 (2014-07-24) paragraphs [0020], [0063]	1-11	A	CO ₂ Electrorreduction in Ionic Liquids, frontiers in Chemistry, 2019 pp. 1-8	1-18
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X	Preliminary Study of CO ₂ Electrolysis in Ionic Liquid. 49th International Conference on Environmental Systems, 2019 pp. 2-6	12-18																
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A	CO ₂ Electrorreduction in Ionic Liquids, frontiers in Chemistry, 2019 pp. 1-8	1-18																
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Date of the actual completion of the international search 10 March 2022	Date of mailing of the international search report 22 March 2022																	
Name and mailing address of the ISA/JP Japan Patent Office (ISA/JP) 3-4-3 Kasumigaseki, Chiyoda-ku, Tokyo 100-8915 Japan	Authorized officer Telephone No.																	

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/JP2022/005734

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
JP	2016-89230	A	23 May 2016	(Family: none)	
US	2014/0202874	A1	24 July 2014	(Family: none)	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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- JP 2016089230 A [0005]