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(54) Title: GLASSY CARBON CONTAINING METAL PARTICLES

(57) Abstract

Glassy carbons including a dispersion of metal particles having a small particle size, their synthesis, and their use in electrochemical cells are described.

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GLASSY CARBON CONTAINING METAL PARTICLES

Background of the Invention

The invention relates to glassy carbon.

Glassy carbon has a unique combination of properties, including chemical and thermal inertness, hardness, impermeability to gases and liquids, and electrical conductivity. Because of these properties, glassy carbon commonly is used in carbon electrodes.

It is known to use oligomers containing acetylene groups as starting materials for making glassy carbon.

Summary of the Invention

In general, the invention features, in one aspect, glassy carbon containing a dispersion of metal particles having an average size of less than 1 micron.

The invention features, in another aspect, an electrochemical cell in which one of the electrodes includes glassy carbon containing a dispersion of metal particles having an average particle size of less than 1 micron.

The invention features, in another aspect, an electrochemical cell in which one or both of the electrodes includes glassy carbon containing a dispersion of metal particles having a relatively uniform size distribution. By relatively uniform size distribution, it is meant that the diameter of 70% of the metal particles are less than 5 times (more preferably 3 times) the number average diameter of the particles.

The invention features, in another aspect, a method of producing glassy carbon containing metal particles. The method involves heating a metal complexed to a molecule (preferably including acetylene groups) for a sufficient period of time for the molecule to cross-link to provide glassy carbon. Preferably, cross-linking is performed at temperatures of less than 1000°C, more

preferably less than 750°C most preferably less than 600°C. The glassy carbon can be incorporated into an electrode for an electrochemical cell.

The invention features, in another aspect, a method of producing a cross-linked carbon matrix that includes metal particles. The method includes providing a metal complexed to a molecule capable of cross-linking to form an sp^2-hybridized carbon matrix, and cross-linking (preferably by heating) the molecules sufficiently to form an sp^2-hybridized carbon matrix having microcrystalline graphite domains having average lattice dimensions of between 1 and 20 nanometers (more preferably between 2.5 and 7.5 nanometers).

The invention features, in another aspect, a method of producing a cross-linked, conductive carbon matrix. The method includes providing a metal complexed to a molecule capable of cross-linking to form a conductive sp^2-hybridized matrix, and cross-linking (preferably by heating) the molecules sufficiently to form an sp^2-hybridized carbon matrix having a conductivity of at least 0.01 s/cm (more preferably at least 0.1 s/cm).

Other aspects of the invention include using glassy carbon containing a dispersion of small metal particles to catalyze a chemical reaction (e.g., reforming, hydrogenations, dehydrogenations, isomerizations of hydrocarbons, oxidations, reductions, and pollutant removal), or to catalyze an electrochemical reaction in an electrochemical cell (e.g., a fuel cell, a cell for electrochemical synthesis, or a sensor).

The preferred metals are transition metals that have desirable catalytic or electrocatalytic properties, for example, platinum, palladium, iron, cobalt, and silver. The preferred molecules are oligomers that include diacetylene and aromatic groups. Preferably the

particles have an average size of less than 100 nanometers, more preferably less than 15 nanometers, most preferably less than 5 nanometers. The preferred glassy carbon has a carbon content of at least 80%.

Glassy carbon is a form of sp^2-hybridized carbon composed of branched and entangled graphite ribbons. The structure and properties of glassy carbon are well known in the art, and are described, for example, in conventional texts such as Kinoshita, Carbon: Electrochemical and Physiochemical Properties (Wiley: New York, 1988) As is recognized by these skilled in the art, although glassy carbon is a well-known material, its properties vary somewhat based on the specific mode of preparation. For example, glassy carbons in general have good conductivity, but some forms have better conductivity than others.

The incorporation of metals on the molecular level in a carbon precursor, followed by cross-linking, results in a conductive, dimensionally stable glassy carbon matrix containing metal particles of controlled composition, size, and catalytic activity. In particular, the size of the metal particles is readily regulated by controlling the initial loading of the metal in the complex; the lower the atom percent of metal in the starting complex (preferably less than 10%, more preferably less than 5%), the smaller the resultant particle size. The small particle size makes a large surface area of metal available for participation in, for example, electrochemical or catalytic reactions. The invention thus provides a highly efficient mode of delivery for catalytic metals, most of which are very expensive. Moreover, acetylenic chemical precursors of glassy carbons are soluble in organic solvents, which makes them easy to handle and form into desired shapes, such as thin films or coatings on the outside of

conventional carbon electrodes. Importantly, the amount of metal in the coating can be controlled by the dilution of the complex in the solution; the more dilute the complex, the thinner the coating formed. Additionally, the cross-linking of the acetylene precursors occur at relatively low temperatures. Also, the invention provides a convenient way to introduce more than one type of metal into glassy carbon, for example, by mixing acetylenic molecules complexed to different metals together prior to cross-linking.

Other features and advantages of the invention will be apparent from the Description of the Preferred Embodiment thereof, and from the claims.

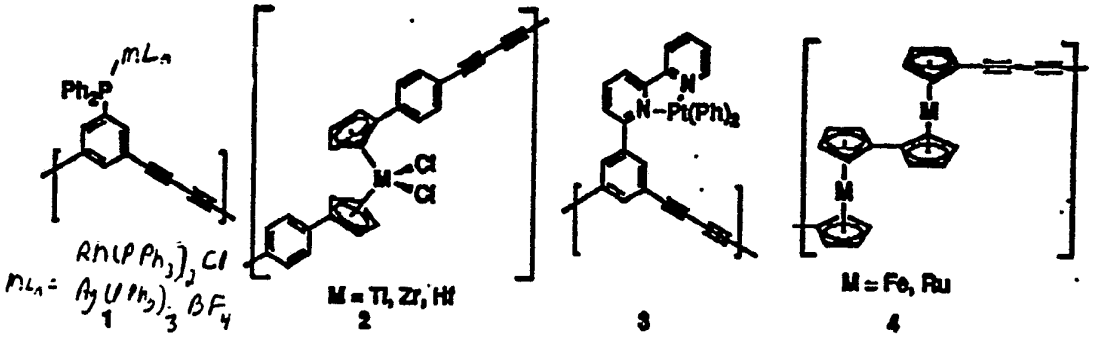
Description of the Preferred Embodiment

The preferred glassy carbon are prepared from aromatic acetylene molecules, typically oligomers or even larger polymers, complexed to a transition metal. Heteroatoms such as nitrogen or boron can be included in the glassy carbon as part of the aromatic ring. Other heteroatoms such as halides or silicon can be substituted for a hydrogen atom in the aromatic ring.

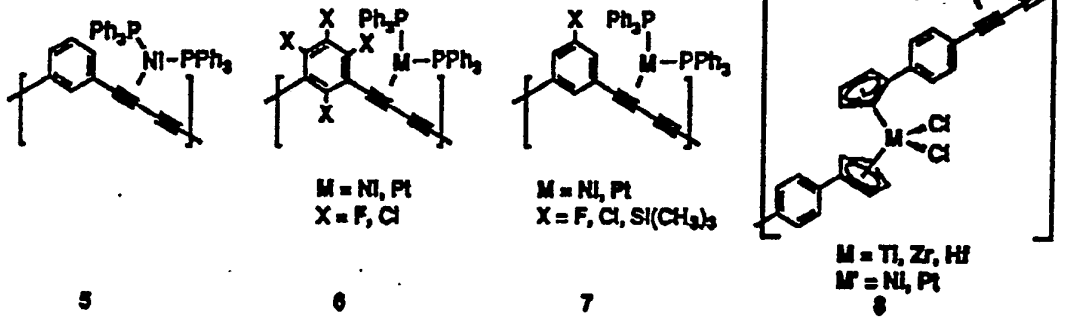
The acetylene groups cross link at a low temperature (e.g., less than 400°C) to form a highly cross-linked carbon network. Further heating at temperatures typically less than 600°C causes the microcrystalline lattice to increase in size. The transition metals can complex to either the acetylene groups, or aromatic rings, or other complexing groups included in the molecule, and are released from the complex during the cross-linking process. The metal remains trapped in the glassy carbon network as small particles of a relatively uniform size. The transition metal selected will depend on the catalytic, or electrocatalytic, properties desired, but can be, for example, platinum, palladium, titanium, ruthenium,

zirconium, hafnium, iron, nickel, and silver, or combinations of these metals, if desired.

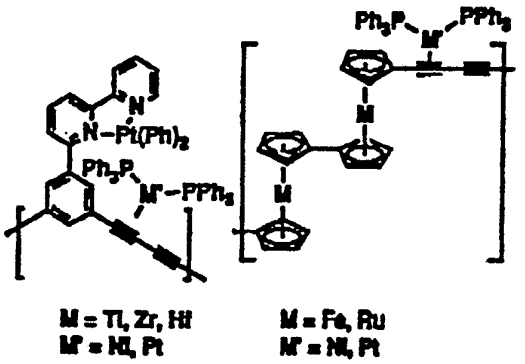
Examples of acetylenic oligomers that are suitable for complexing with transition metals to provide precursors for glassy carbon are legion, and are well-known to those skilled in the art. Representative examples of suitable complexed oligomeric precursors include those having formula 1-10, below. The oligomers may be end-capped with mono-functional acetylenes (not shown). The illustrated repeat unit of the oligomers is shown complexed to the metal; usually in the full oligomer, only a portion of the repeat units are complexed to metal atoms, depending on the metal loading into the reaction mixture that generated 1-10.



1 2 3 4

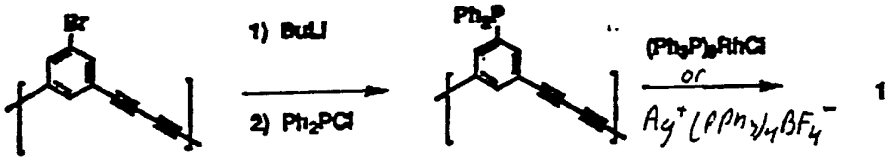


5 6 7 8

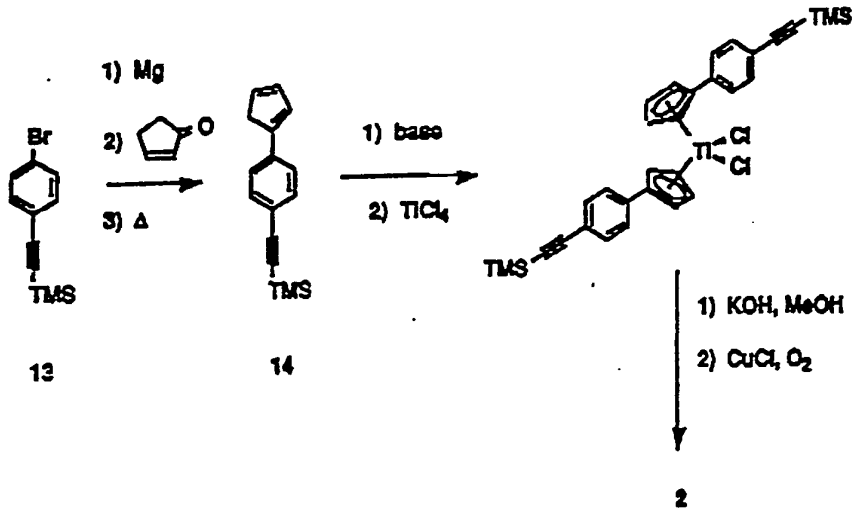


9 10

Oligomers 1-10 can be prepared by standard chemical procedures. For example, the synthesis of 1 can be accomplished by reaction of 11 with butyllithium followed by reaction with chlorodiphenylphosphine to give 12. Reaction of 12 with $(PPh_3)_3RhCl$ or $Ag(PPh_3)_4BF4$ gives 1.



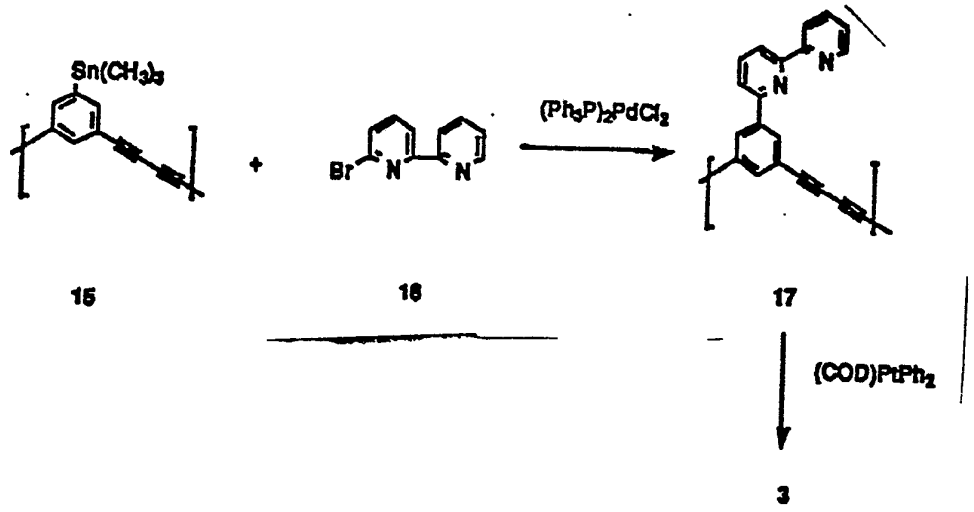
The synthesis of 2 can be accomplished by treatment of 13 with magnesium in diethyl ether, followed by reaction with cyclopentenone, followed by dehydration to give a general cyclopentadiene ligand which can be used for complexation with various metals.



Treatment of 14 with base, such as butyllithium or sodium hydride, and reaction with $TiCl_4$ gives the diacetylene metal complex. The removal of the trimethylsilyl groups can be accomplished with catalytic potassium or sodium hydroxide in methanol or tetrahydrofuran containing water

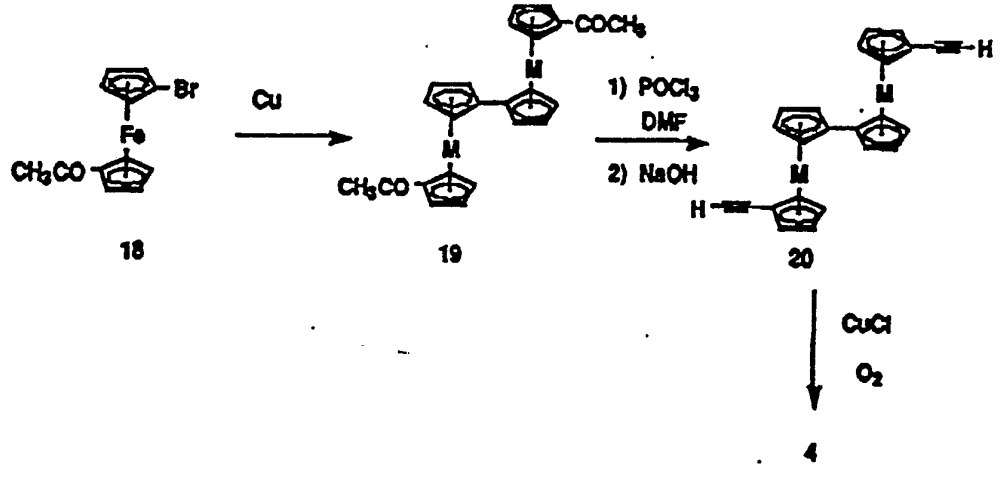
and the oligomer or polymer can be prepared by subsequent reaction with oxygen and copper chloride in *o*-dichlorobenzene in the presence of an amine base to give 2.

Platinum complex 3, which serves as a precursor to metal doped glassy carbon containing a bypyridyl ligand complexed with platinum, can be prepared by reaction of 15 with 16 using bis(triphenylphosphine)palladium(II) chloride as a catalyst in toluene to give 17. Reaction of 17 with (cyclooctadiene)diphenylplatinum(II) gives 3.



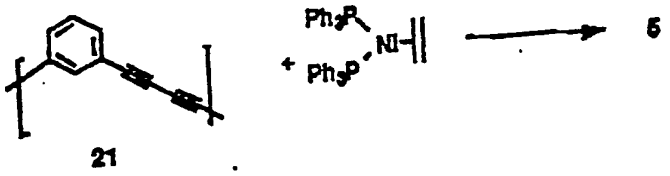
15 16 17 3

The complex containing iron 4 can be prepared by reaction of 1,1'-bromoacetylferrocene (18) with copper to give 19. Treatment of 19 with $POCl_3$ in dimethylformamide followed by reaction with sodium hydroxide gives 20. Reaction of 20 in the presence of copper chloride and oxygen gives 4.



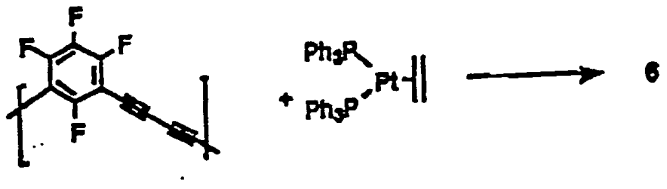
18 19 20 4

Glassy carbon precursor 5, which contains nickel, can be prepared by reaction of 21 with ethylene bis(triphenylphosphine)nickel(0).

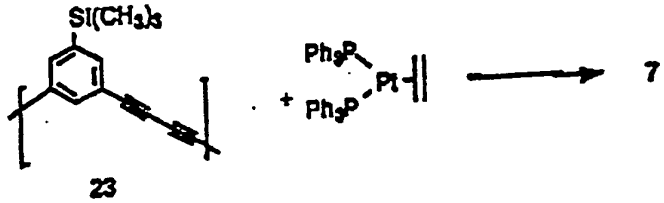


21

A complex that also includes fluorine (6) can be made by treatment of 23 with ethylene bis(triphenylphosphine)platinum(0) to give 6 with X = F and M = Pt. Similarly, the treatment of 24 with ethylene bis(triphenylphosphine)platinum(0) gives 7 with X = $Si(CH_3)_3$ and M = Pt.

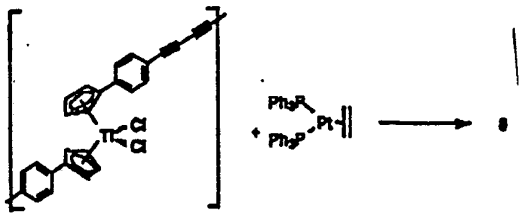


22

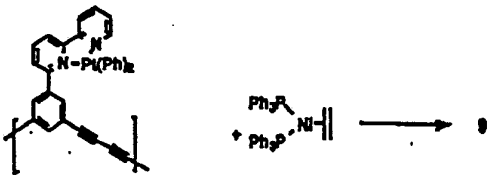


23

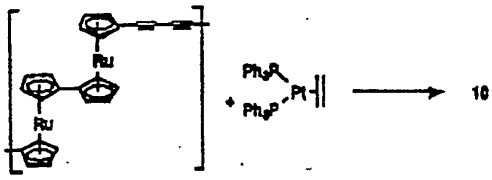
The starting complex can also include more than one metal. For example, complex 8 can be prepared by reaction of 2 with ethylene bis(triphenylphosphine)platinum(0) to give 8 with M = Ti and M′ = Pt. Similarly, the treatment of 3 with ethylene bis(triphenylphosphine)nickel(0) gives 9 with M′ = Ni. The treatment of 4 with M = Ru with ethylene bis(triphenylphosphine)platinum(0) gives 10 with M = Ru and M′ = Pt.



2



3



The above examples are only representative, and many other suitable complexes, and procedures for making them, are known in the art. For example, the molecular weight of the oligomers and polymers can be controlled by suitable use of end-capping groups such as phenyl acetylene, pentafluoroacetylene and the like when the molecules are prepared. The level of metal incorporated in these molecules also can be controlled by the amount of metal complex added to the acetylene molecule. In addition, glassy carbon containing a dispersion of two or more types of metal particles also can be prepared by simply mixing different metal containing oligomeric complexes prior to cross-linking and annealling.

The most preferred glassy carbons include a dispersion of platinum particles. Platinum is a catalyst for many important chemical reactions, including oxygen and hydrogen reduction. Glassy carbon including the dispersion of platinum particles can be used, for example, in oxygen/hydrogen or methanol/oxygen fuel cells. It is highly suitable for these uses because the platinum is provided efficiently in a stable matrix.

The preferred glassy carbons containing platinum particles were prepared according to the following procedures.

Ethylene bis(triphenylphosphine)platinum(0)

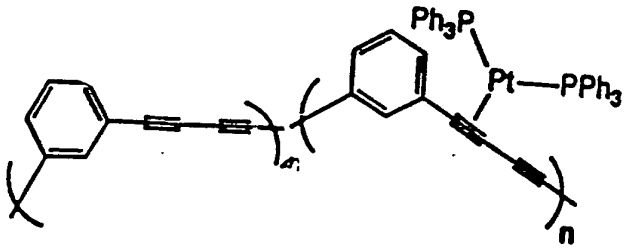
Ethylene bis(triphenylphosphine)platinum(0) was prepared by a three-step process.

Triphenylphosphine (1.46 g, 5.6 mmol) was dissolved in 20 mL of absolute ethanol at 65°C. When the solution was clear, 0.14 g (0.0025 mol) of potassium hydroxide in 1 mL of water and 4 mL of ethanol was added. To this was then added 0.5 g (1.2 mmol) of potassium tetrachloroplatinate(II) dissolved in 5 mL of water while stirring at 65°C. A pale yellow solid precipated within a few minutes of the first addition. After cooling, the compound was recovered by filtration, washed with 50 mL of warm ethanol, 20 mL of water and 12 mL of cold ethanol to give 1.17 g (78 %) of product.

Carbon dioxide and oxygen were bubbled through a solution of 1.17 g (0.9 mmol) of tetrakis(triphenylphosphine)platinum(0) in 30 mL of benzene. After 45 min the mixture turned pale yellow and a solid precipated. The solid was recovered by filtration and washed with benzene. The crude product was dissolved in 20 mL of dichloroethane and 0.47 g (1.8 mmol) of triphenylphosphine was added. The mixture was refluxed overnight. To the mixture, 20 mL of benzene was added and the volume was reduced by half *in vacuo*. White crystals were recovered by filtration, washed with benzene and ethanol to give 0.63 g (77 %) of product.

A suspension of 0.61 g of $[Pt(PPh_3)_2CO_3]\cdot C_6H_6$ in 20 mL of ethanol, under a stream of ethylene, was stirred rapidly. To this solution, 8 mL of 0.1 *M* (0.031 g. 0.8 mmol) of sodium borohydride in ethanol was added dropwise for a period of 30 minutes. The white solid (0.442 g, 81 % yield) was recovered by filtration, washed with 10 mL of ethanol, 10 mL of water, and finally with 10 mL of ethanol, and dried *in vacuo*.

Poly[(phenylene diacetylene)
bis(triphenylphosphine)platinum(0)]



By varying the ratio of ethylenebis (triphenylphosphine)platinum(0) to poly(phenylene diacetylene) a series of complexes having the above formulae were prepared with different platinum levels. The complexes can be used to produce glassy carbon without further modification.

(a) Platinum:diyne ratio 1:2

In 25 mL of toluene 0.3 g (0.4 mmol) of ethylene bis(triphenylphosphine) platinum(0) was dissolved with 0.1 g (0.8 mmol of phenyldiyne unit) of poly(phenylene diacetylene). The mixture was heated to 65°C for 6 hours. After 2 hours, the solution turned from pale yellow to dark brown. This solution was poured into 250 mL of petroleum ether and a solid precipitated. The oligomer (0.270 g, 69 %) was recovered by filtration and washed with ethanol.

(b) Platinum:diyne ratio 1:4

In 25 mL of toluene 0.15 g (0.2 mmol) of ethylene bis(triphenylphosphine) platinum(0) was dissolved with 0.1 g (0.8 mmol of phenyldiyne unit) of poly(phenylene diacetylene). The mixture was heated to 65°C for 6 hours. After 2 hours, the solution turned from pale yellow to dark brown. This solution was poured into 250 mL of petroleum ether and a solid precipitated. The

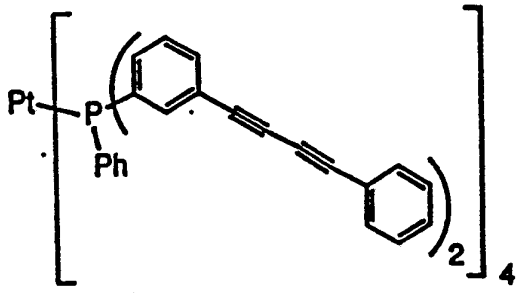
oligomer (0.10 g, 60%) was recovered by filtration and washed with ethanol.

(c) Platinum:diyne ratio 1:6

In 25 mL of toluene 0.1 g (0.13 mmol) of ethylene bis(triphenylphosphine) platinum(0) was dissolved with 0.1 g (0.8 mmol of phenyldiyne unit) of poly(phenylene diacetylene). The mixture was heated to 65°C for 6 hours. After 2 hours, the solution turned from pale yellow to dark brown. This solution was poured into 250 mL of petroleum ether and a solid precipitated. The oligomer (0.05 g, 60 %) was recovered by filtration and washed with ethanol.

Tetrakis[bis[1-(3-phenylbutadiynyl)phenyl] phenylphosphine]platinum(0)

An alternative starting complex, tetrakis[bis[1-(3-phenylbutadiynyl)phenyl]phenylphosphine]platinum(0), which has the below formula, was prepared in two steps.



First, to 3 g (10 mmol) of (1-bromo-3-phenylbutadiynyl)benzene dissolved in 65 mL of tetrahydrofuran, 7 mL (11 mmol) of n-butyllithium (1.6 *M* in hexanes) was added slowly to the solution at -78°C. The solution turned dark brown after 5 minutes. The

solution was stirred at -78°C for 2 hours and then 0.71 mL (5.3 mmol) of dichlorophenylphosphine was added slowly. The solution immediately turned yellow. The solution was allowed to warm to room temperature and to stir overnight. The reaction was quenched with a saturated solution of ammonium chloride, the solids removed by decantation, and the organic layer was washed with ammonium chloride solutions and dried with anhydrous magnesium sulfate. After filtration of the solid, the solvent was removed *in vacuo*, and the yellow residue was purified by column chromatography on silica gel (20% CH_2Cl_2 in hexanes) to give 0.7 g (20 %) of light white crystals.

The bis[1-(3-phenylbutadiyne)phenyl]phenylphosphine (0.47 g, 0.09 mmol) was dissolved in the minimum amount of benzene (4 mL) and then diluted in 10 mL of ethanol. The solution was heated to 65°C and when the solution turned clear, 0.5 mL of a solution of 0.21 g (0.004 mol) of potassium hydroxide in 1 mL of water and 4 mL of ethanol was added. To this, was then added dropwise, 0.0832 g (0.2 mmol) of potassium tetrachloroplatinate(II) dissolved in 5 mL of water, while stirring at 65°C. After the first drops, the solution became cloudy, and a yellow solid precipitated. The solid (0.129 g, 51 %) was recovered by filtration and washed with 20 mL of warm ethanol, 10 mL of water and 15 mL of ethanol.

Glassy Carbon

The acetylenic complexes described above can be converted to glassy carbon at relatively low temperatures. The initial heating causes the acetylene groups to cross-link, forming a highly cross-linked carbon matrix. The cross-linking can be carried out at temperatures below 500°C (e.g., 350°C). Upon further

heating, the cross-linked matrix anneals, to provide glassy carbon. Annealization typically requires heating at a higher temperature (e.g., 550°C - 700°C) than the initial cross-linking. Both steps can be carried out simultaneously by simply heating at the higher temperature.

Preferably the glassy carbons should have a conductivity greater than 0.01 s/cm, more preferably greater than 0.1 s/cm, and most preferably greater than 0.7 s/cm. The microcrystalline graphite dimensions, as determined by conventional Raman spectroscopy and X-ray powder diffraction techniques, are between 1 and 20 nanometers, more preferably greater than 2 nanometers, most preferably between 2.5 and 7.5 nanometers. The glassy carbon electrode should function as a practical electrode. Preferably, in cyclic voltametry of ferris ferrocyanide, the oxidation-reduction separation should be $\Delta Ep < 200$ mV, more preferably <150mV, and most preferably <100mV.

The conversion of the platinum-complex precursors to glassy carbon was performed by alternative procedures, one which resulted in pellets of glassy carbon, the other which resulted in a film on a pre-existing glassy carbon disc and on carbon felt.

a) **Glassy carbon pellets**

Glassy carbon pellets were made in two steps. Approximately 150 mg of a precursor were submitted to a pressure of 3500 psi at a temperature of 350°C for 2 hours in a 1 cm diameter steel die. A Carver laboratory press model C was used. The sample was allowed to cool slowly. At the end of this period, a 1 cm diameter black disc of cross-linked carbon solid was obtained. The pellets were then sealed *in vacuo* in a quartz tube and heated to 600°C at a rate of 1°C/min for a total period

of 15 hours in a Thermolyne type 6000 furnace, and then allowed to cool at a rate of 1°C/min to room temperature.

b) Glassy carbon films

A toluene solution of a precursor was spin-coated (Headway Research, PWM101 model) on an Atomergic V25 glassy carbon disc. The solvent was evaporated and the disc was sealed *in vacuo* and thermally treated to 600°C under the same conditions as that for the pellets. A similar procedure can be used to coat a variety of materials, including carbon felt, carbon filters, other metals, silica, and alumina. Importantly, this provides the uses with the ability to take a variety of backings and turn them into, e.g., a platinum electrode, by simple coating procedures.

Raman analysis confirms the glassy carbon microcrystalline structure of these carbon solids exhibiting bands at approximately 1580 cm^{-1} and 1360 cm^{-1}, consistent with the formation of an sp^2-hybridized carbon lattice. X-ray photoelectron spectroscopic analyses and microprobe analysis confirmed the incorporation of approximately 0.5 to 1 atom % of platinum(0) in glassy carbon.

The size of platinum particles can be determined by standard transmission microscopic analysis. For example, a thin film of the glassy carbon containing dispersed platinum particles was prepared by evaporation of a glassy carbon precursor onto a sodium chloride disc to give a 2-3 micron thick coating. The disc was then heated to 600°C to provide a film of glassy carbon. The film was then lifted from the disc, and a transmission electron micrograph of the edge of the film is taken, and the diameters of the particles (or clusters) are recorded, and a mean obtained. The average platinum particle size in the glassy carbons obtained from the

previously described precursors in the range of 1.4 to 2.1 nanometers.

H^+ Reduction

(a) The glassy carbons of the invention are useful in a wide variety of catalytic and electrochemical applications. For example, glassy carbon containing dispersed platinum particles, when used in place of platinum in a platinum disc electrode and studied for its effect on the reduction of H^+ to H_2, exhibited a performance close to that of a pure platinum disc.

(b) An electrode was also prepared by applying 5 drops of a saturated solution of a 1:2 platinum:diyne ratio of poly[(phenylenediacetylene) bis(tri-phenylphosphine) platinum(0)] in toluene to each side of a carbon felt electrode, which consisted of a matrix of carbon fibers. The electrode was heated under vacuum to 600°C (1°C/min), and cured at 600°C for 6 hours to provide the glassy carbon. The resulting electrode was used in place of a standard platinum disc electrode. Voltrametry was taken in a 1M H_2SO_4 solution at different scan rates in the range of 0.2V to -0.6V versus a conventional Ag/AgCl reference electrode.

(c) The activity of the platinum dispersed in glassy carbon was compared to a polycrystalline platinum electrode for H^+ reduction over time at constant potential. A 1 atom % platinum in glassy carbon thin film on conventional glassy carbon was held at constant potential of -0.044V vs NHE in 1 molar $HClO_4$ solution for a period of 60 min. The current density of the 1 atom % platinum containing glassy carbon exhibited a higher current density than did a polycrystalline platinum electrode mounted in glass at times greater than 10 min.

O_2 Reduction

The activity of the platinum dispersed in glassy carbon was compared to a polycrystalline platinum electrode and a conventional glassy carbon electrode for oxygen reduction. A 1 atom % platinum in glassy carbon thin film on conventional glassy carbon was exposed to oxygen in 1M $HClO_4$ buffer and scanned at 50 mV/sec from 1.0 to -0.5 V vs SSCE. The current density and potential for O_2 reduction with the platinum in glassy carbon electrode exhibited a performance close to that of a pure platinum disc. In the case of the carbon felt electrode including a thin coating of glassy carbon containing platinum particles, the porosity, stability, and catalytic efficiency of the electrode should be very useful for electrochemical applications.

Other embodiments are within the claims. For example, glassy carbons containing metal particles other than platinum can be prepared by cross-linking and annealling complexes having formula 1, 2, 4, 5, 6 (M=Ni), 7 (M=Ni), 8, 9, and 10. Moreover, glassy carbons containing heteroatoms such as N can be prepared, for example, by cross-linking and annealling a complex having formulae 3.

Glassy carbons containing dispersions of metal particles can be prepared from acetylenic oligomers lacking aromatic groups, for example, some of the acetylenic oligomers described in Hay, U.S. 3,332,916, which is hereby incorporated by reference. In addition, the glassy carbons can be prepared from other, non-acetylenic precursors, such as phenolic formaldehyde oligomers, that are complexed to a metal.

O_2 Reduction

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Claims

1. A material comprising glassy carbon including a dispersion of metal particles having an average size of less than 1 micron.

2. The material of claim 1, wherein said metal particles have an average size of less than 300 nanometers.

3. The material of claim 2, wherein said metal particles have an average size of less than 100 nanometers.

4. The material of claim 3, wherein said metal particles have an average size of less than 50 nanometers.

5. The material of claim 4, wherein said metal particles have an average size of less than 15 nanometers.

6. The material of claim 5, wherein said metal particles have an average size of less than 10 nanometers.

7. The material of claim 6, wherein said metal particles have an average size of less than 5 nanometers.

8. The material of claim 7, wherein said metal particles have an average size of less than 3 nanometers.

9. The material of claim 1, where said glassy carbon includes a dispersion of transition metal particles.

10. The material of claim 9, wherein said transition metal particles are platinum.

11. The material of claim 9, wherein said transition metal particles are silver.

12. The material of claim 9, wherein said transition metal particles are palladium.

13. The material of claim 9, wherein said transition metal particles are iron.

14. The material of claim 9, wherein said transition metal particles are copper.

15. The material of claim 9, wherein said glassy carbon has a carbon content of at least 70 atom percent.

16. The material of claim 15 wherein said glassy carbon has a carbon content of at least 80 atom percent.

17. The material of claim 1, wherein said material is a film.

18. The material of claim 17, wherein said material is a film having a thickness of less than 10 microns.

19. An electrochemical cell comprising an anode and a cathode, wherein said anode or said cathode comprises glassy carbon including a dispersion of platinum particles having an average particle size of less than 50 nanometers.

20. An electrochemical cell comprising an anode and a cathode, wherein said anode or said cathode comprises glassy carbon including a dispersion of metal particles having an average particle size of less than 1 micron.

21. The electrochemical cell of claim 20, wherein said average particle size is less than 100 nanometers.

22. The electrochemical cell of claim 21, wherein said average particle size is less than 25 nanometers.

23. The electrochemical cell of claim 22, wherein said average particle size is less than 10 nanometers.

24. The electrochemical cell of claim 20, wherein said particles have a relatively uniform size distribution.

25. The electrochemical cell of claim 20, wherein said anode or said cathode comprises a film of glassy carbon.

26. A material comprising glassy carbon including a dispersion of metal particles having a relatively uniform size distribution.

27. An electrochemical cell comprising an anode and a cathode, wherein said anode or said cathode comprises glassy carbon including a dispersion of metal particles having a relatively uniform size distribution.

28. A method of producing glassy carbon containing metal particles, comprising

providing a metal complexed to a molecule capable of cross-linking to form a glassy carbon; and

heating said metal complex for a sufficient period of time for said molecule to cross-link to form glassy carbon containing metal particles.

29. The method of claim 28, wherein said molecule includes an acetylene group.

30. The method of claim 28, wherein said metal complex is cross-linked to provide glassy carbon at a temperature of less than 1000°C.

31. The method of claim 28, wherein said molecule is a polymer including aromatic groups.

32. The method of claim 30, wherein said metal complex is cross-linked to provide glassy carbon at a temperature of less than 750°C.

33. The method of claim 30, wherein said metal complex is cross-linked to provide glassy carbon at a temperature of less than 600°C.

34. The method of claim 28, wherein said metal is a transition metal.

35. A method of producing an electrochemical cell, comprising

providing a metal complexed to a molecule capable of cross-linking to form glassy carbon;

cross-linking said molecule to form glassy carbon containing metal particles;

incorporating said glassy carbon into an electrode; and

using said electrode in an electrochemical cell.

36. The method of claim 35 wherein said cross-linking comprises heating said molecule.

37. The method of claim 35 wherein said metal particles have an average size of less than 1 micron.

38. The method of claim 35 wherein said molecule includes an acetylene group.

39. A method of producing glassy carbon including a dispersion of metal particles, comprising

providing a metal complexed to a molecule capable of cross-linking to form glassy carbon; and

cross-linking said molecule to provide glassy carbon including a dispersion of particles of said metal.

40. The method of claim 39, wherein said molecule includes an acetylene group.

41. The method of claim 39, wherein said metal has a particle size of less than 100 nanometers.

42. A method of producing an electrochemical cell, comprising

providing glassy carbon including a dispersion of metal particles having a size of less than 1 micron;

incorporating said glassy carbon into an electrode; and

using said electrode in an electrochemical cell.

43. The method of claim 42, further comprising using said electrochemical cell as a fuel cell.

44. The method of claim 42, further comprising using said electrochemical cell for electrochemical synthesis.

45. The method of claim 42, further comprising using said electrochemical cell as a sensor.

46. A method of catalyzing a chemical reaction, comprising

providing glassy carbon including a dispersion of metal particles; and

catalyzing a chemical reaction with said metal particles.

47. The method of claim 46, wherein said chemical reaction comprises reforming.

48. The method of claim 46, wherein said chemical reaction comprises a hydrogenation.

49. The method of claim 46, wherein said chemical reaction comprises a dehydrogenation.

50. The method of claim 46, wherein said chemical reaction comprises an isomerization of hydrocarbons.

51. The method of claim 46, wherein said chemical reaction comprises an oxidation.

52. The method of claim 46, wherein said chemical reaction comprises reduction.

53. The method of claim 46, wherein said chemical reaction comprises pollutant removal.

54. A method of producing a cross-linked carbon matrix including metal particles, comprising

providing a metal complexed to a molecule capable of cross-linking to form an sp^2-hybridized carbon matrix; and

cross-linking said molecule sufficiently to form an sp^2 hybridized carbon matrix having microcrystalline graphite domains having lattice dimension of between 1 nanometer and 20 nanometers.

55. The method of claim 54, wherein said lattice dimensions are between 2.5 nanometers and 7.5 nanometers.

56. A method of producing a cross-lined, conductive carbon matrix, comprising,

providing a metal complexed to a molecule capable of cross-linking to form a conductive sp^2-hybridized carbon matrix; and

cross-linking said molecule sufficiently to form an sp^2-hybridized carbon matrix having a conductivity of at least 0.01 s/cm.

57. An electrode comprising a thin film of glassy carbon including a dispersion of transition metal particles having an average particle size of less than 1 micron.

58. The electrode of claim 57, further comprising a carbon fiber onto which said film is coated.

59. The electrode of claim 57, further comprising a carbon felt onto which said film is coated.

60. The electrode of claim 57, further comprising metal, silica, or aluminum onto which said film is coated.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/06458

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
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)

U.S. : Please See Extra Sheet.

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

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

USPAT: electrode, anode, cathode; glossy carbon; platinum, Pt, silver, rg, palladium, Pd, Iron, Fe, Copper, Cu, cross-link?; Silica, Aluminium, Al; Acetylene

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US,A, 4,970,189 (Tachibana) 13 November 1990 (See Column 2, lines 14-36, column 3, lines 1-15, Claims 2 and 3.)	1-17; 26,28,30-31,34,39,41,46 18-25, 27,29,32-33,35-38, 40,42-45,47-60
X Y	US,A, 4,518,488 (Wennerberg) 21 May 1985 (See Col. 10, lines 8-12 and lines 24-25 and Col. 11, lines 44-45.)	1-6,9-16,26,28,30-31,39,41,46 7-8,17-25,27,29,35-38, 40,42-45,47-60

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 29 SEPTEMBER 1992	Date of mailing of the international search report 16 NOV 1992
Name and mailing address of the ISA/ Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer KATHRYN GORGOS for Telephone No. (703) 308-3328

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/06458

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	Yoshuda, "New Carbon Composites Containing Ultra furo re, co or ni particles. 1. Facile Synthesis by Pyrolysis of Organometallic Polymers", Journal of Inorganic and organometallic Polymers, vol. 1, No. 1, 1991, pg. 135-141 (see pages 135-137.)	1-3,9,13-14,26-28,30-31,34-36,39,41-46 4-8,10-12,15-25,29,32-33, 37-38,40,47-60

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/06458

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (5):

C25B 11/12, 9/00, 1/00, 3/00; C25F C09K 3/00; HO1B 13/00; C07C 5/00, 5/02, 5/22, 5/32, 27/10; C10G 1/00, 35/04, 45/00; H01M 4/88, 4/86, 4/90, 4/92, 4/96 B01J 21/18, 23/40, 23/74

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

182.13, 182.14, 182.15, 182.16, 423/DIG 13; 585/250, 440; 208/3,48,134,143; 502/101,180,185; 429/40,44; 106/286.1,286.3,286.7

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

182.13, 182.14, 182.15, 182.16, 423/DIG 13; 585/250, 440; 208/3,48,134,143; 502/101,180,185; 429/40,44; 106/286.1,286.3,286.7
C25B 11/12, 9/00, 1/00; H01M 4/86, 4/88 4/92, 4/90, 4/96